CALCULATIONS IN
PHYSICAL CHEMISTRY

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BY

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PREFACE

An adequate training in working numerical problems in Physical Chemistry is generally recognized as an essential adjunct to courses in this subject, and many lecturers, in common with the present authors, must have felt that a small manual covering the more advanced work would be useful both to them and to the students. There are several works of a more elementary character, and no attempt has been made to cover this ground again, although the book is reasonably complete in itself. On the other hand, very specialized or difficult types of calculations (e.g. those dealing with the quantum theory of reaction velocity and applications of statistical mechanics) have been purposely omitted. Exigencies of space are responsible for the curtailment or deletion of many sections, e.g. on activity and on various equations of state.

The theoretical sections are mainly collections of working formulæ, but attention has been given to matters which experience has shown are likely to offer difficulties to students, e.g. the units involved. Especial care has been taken to emphasize the differences between European and American nomenclature where these exist. It is hoped that this will assist students when referring to the many excellent American text-books on physical chemistry.

Beyond the object set out above the work has no pretensions, but it is thought possible that it may also prove useful as a companion to students beginning research in physical chemistry.

The exercises are nearly all taken directly from the litera-
ture, although acknowledgments are due to the authorities of
Manchester University, to the Senate of London University,
and to the Registrary of Cambridge University for permission
to reproduce examination questions. A collection of problems
of the standard set in the B.Sc. Special (Honours) Examina-
tion of the University of London is provided at the end of
the book. These are intended for homework and no answers
are given.

The authors have great pleasure in thanking Dr. A. Ferguson
and Dr. D. C. Jones for useful suggestions, Mr. A. Brewin,
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CALCULATIONS IN PHYSICAL CHEMISTRY

Mathematical Introduction[*]

(a) CALCULUS

(1) Standard Forms.

The *differential coefficient* (or *derivative*) of $y = f(x)$ with respect to x (written dy/dx or $f'(x)$) is the rate of increase of y with respect to x. It represents the slope of the tangent to the curve $y = f(x)$ at the point x. The process of finding $f(x)$ from $f'(x)$ is known as *integration*: $\int f'(x)dx = f(x) + c$, where c is an integration constant. See *H. M.*, p. 135.

In the following standard forms n and a are constants, u and v functions of x; the constant c is omitted from the integrals.

dy	$a\,dx$	0	$nx^{n-1}\,dx$	$-x^{-2}\,dx$	$u\,dv + v\,du$	$e^x\,dx$	$a^x \ln a\,dx$
$y = f(x)$	ax	a	x^n	x^{-1}	uv	e^x	a^x
$\int y\,dx$	$\frac{1}{2}ax^2$	ax	$x^{n+1}/(n+1)$	$\ln x$	—	e^x	$a^x / \ln a$

[*] For further details see Partington, *Higher Mathematics for Chemical Students*, London, 1920 (referred to as *H. M.*); Bisacre, *Applied Calculus*, 1921; F. Daniels, *Mathematical Preparation for Physical Chemistry*, 1928. A summary of chemical mathematics is given in Eucken, Jette, and La Mer *Fundamentals of Physical Chemistry*, New York, 1925, pp. 1–34. See also Running, *Empirical Formulas*, 1917.

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Note.—If $a^x = y$ then $\ln_a y = x$. If $e = 2.71828$, $\log_e a = 2.3026 \log_{10} a$, or $\log_{10} a = 0.4343 \log_e a$. In the present book $\log_{10} a$ is written $\log a$, and $\log_e a$ is $\ln a$.

(2) Areas bounded by Curves.

The area bounded by the curve $y = f(x)$, the x-axis, and the ordinates $x = x_2$, $x = x_1$, is given by

$$\text{area} = \int_{x_1}^{x_2} y \, dx. \tag{1}$$

When the equation of the curve is unknown the area may be determined by counting the co-ordinate squares or else by an application of Simpson's rule (*H. M.*, p. 211). In (1), x_1, x_2 are the *limits* of the integral; this is a *definite integral*, and the constant c disappears (*H. M.*, p. 183).

EXAMPLE.—The calculation of entropy (p. 32).

(3) Maxima and Minima.

The curve $y = f(x)$ attains a *maximum* or a *minimum* when $dy/dx = 0$. When the point is a maximum the *second derivative* $d^2y/dx^2 < 0$ and when it is a minimum $d^2y/dx^2 > 0$. The value of d^2y/dx^2 is found by differentiating dy/dx with respect to x.

EXAMPLE.—An equation for the "best reading" of an instrument is readily deduced. Let y be the quantity to be measured and x the observed quantity (*i.e.* the reading of the instrument). Let $y = f(x)$; then $dy = f'(x)dx$ and $dy/y = f'(x)dx/f(x)$. The error in y due to an error dx in the reading, x, is $dy/y = u$, say. For the error in y to be as small as possible u must be a minimum. To find the condition determine du/dx and equate to zero: $du/dx = [(f(x)f''(x)dx - f'(x)f'(x)dx)]/[f(x)]^2 = 0$ or $f(x)f''(x) = [f'(x)]^2$, which is the required condition.

Thus in the case of the Wheatstone bridge, if $a =$ length of wire and $x =$ wire reading corresponding with the resistance being measured, y, then $a - x$ is the reading corresponding with the known resistance, r, and $y = f(x) = rx/(a - x)$. Hence $f'(x) = ar/(a - x)^2$ and $f''(x) = 2ar/(a - x)^3$, and the most accurate readings are obtained when $[rx/(a - x)][2ar/(a - x)^3] = [ar/(a - x)^2]^2$ or $x = a/2$, *i.e.* when the reading is near the centre of the bridge.

(b) Solution of Equations

(1) Graphical Method.

In order to solve the equation $f(x) = 0$, $f(x)$ is divided into two parts: $f_1(x) - f_2(x) = 0$. The curves $y = f_1(x)$ and $y = f_2(x)$ are then plotted on the same graph. The co-ordinates of the point (or points) of intersection give the required roots.

(2) Solution of Quadratic Equations.

The roots of the quadratic equation $ax^2 + bx + c = 0$ are given by

$$x = (-b \pm \sqrt{b^2 - 4ac})/2a.$$

(3) Newton's Method.

This is a general method of solving an equation of any degree: $f(x) = 0$. A solution, a, is guessed; suppose this solution to differ from the true solution x by h, a small quantity: $x = a + h$. Then, by Taylor's theorem (*H. M.*, p. 172):

$$0 = f(x) = f(a + h) = f(a) + hf'(a) + h^2f''(a)/2! + \ldots .$$

If h is small, terms involving h to the second and higher powers may be neglected and an approximate value of h obtained from the equation $f(a) + hf'(a) = f(x) = 0$; that is, $h = -f(a)/f'(a)$ and $x = a - [f(a)/f'(a)]$, approx. Let this approximation $= b$; the process is then repeated, so that $x = b + h'$ is obtained, and so on, until the correction h is negligible.

EXAMPLE.—Find one solution of the equation $x^3 - 8x^2 + 7x + 12 \cdot 67 = 0$.

By inspection, $f(2) = 2 \cdot 67$ and $f(3) = -11 \cdot 33$, so that the required solution is between 2 and 3 and is nearer 2. Try $a = 2 \cdot 3$. Then $f(2 \cdot 3) = (2 \cdot 3)^3 - 8(2 \cdot 3)^2 + 7(2 \cdot 3) + 12 \cdot 67 = -1 \cdot 383$; $f'(a) = 3a^2 - 16a + 7 = -13 \cdot 93$. Hence $h = -f(2 \cdot 3)/f'(2 \cdot 3) = -1 \cdot 383/13 \cdot 93 = -0 \cdot 0993$, so that, as a first approximation, $x = a + h = 2 \cdot 3 - 0 \cdot 099 = 2 \cdot 2$ approx. It will be found that $f(2 \cdot 2) = -0 \cdot 002$ which may be near enough to zero for the practical purpose, and $x = 2 \cdot 2$ may be taken as the required root. The number of repetitions required depends on the closeness of the initial estimate to the true solution.*

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* For *nomographic* methods see Deming, *Manual of Chemical Nomography*, 1918.

(c) PARTIAL MOLAL QUANTITIES

(1) General Equations.

The extensive property G (e.g. vol., free energy, &c.) c a solution containing n_1 mols of A, n_2 mols of B, ... depend on T, p, n_1, n_2, ... The *partial molal values* of G for eac constituent, $\bar{G}_1$, $\bar{G}_2$, ... are defined by

$$\bar{G}_1 = (\partial G/\partial n_1)_{p,\,T}, \quad \bar{G}_2 = (\partial G/\partial n_2)_{p,\,T} \quad . \quad . \quad (2)$$

and so on, or (p and T constant):

$$dG = \bar{G}_1 dn_1 + \bar{G}_2 dn_2 + \ldots \quad . \quad . \quad . \quad (3)$$

Since $\bar{G}_1$ and $\bar{G}_2$ depend upon the *relative* amounts of A and B, respectively, they remain constant when n_1 and n_2 are varied in a fixed ratio. Hence

$$G = n_1 \bar{G}_1 + n_2 \bar{G}_2 + \ldots \quad . \quad . \quad . \quad (4)$$

If the differential of (4) is compared with (3) we have:

$$n_1 d\bar{G}_1 + n_2 d\bar{G}_2 + \ldots = 0. \quad . \quad . \quad . \quad (5)$$

The *mol fraction* of A is defined by $N_1 = n_1/(n_1 + n_2 + \ldots)$, so that $N_1 + N_2 + \ldots = 1$. When $n_1 + n_2 + \ldots = 1$, and $N_1 = n_1$, $N_2 = n_2$, &c.,

$$N_1 d\bar{G}_1 + N_2 d\bar{G}_2 + \ldots = 0. \quad . \quad . \quad . \quad (6)$$

The composition of a binary solution may also be expressed in terms of *molality*, M, the number of mols of solute dissolved in 1000 g. of solvent. For a given solution M is independent of T. In a binary solution N_1 usually refers to the solvent.

These equations are due to Gibbs and Duhem.

(2) Graphical Calculation of Partial Molal Quantities.

(i) Plot G against n_1 for fixed values of n_2. The slope of the curve at any point is $dG/dn_1 = \bar{G}_1$. By repeating the process with $n_1 = $ constant, $\bar{G}_2$ is found.

(ii) The value of G per mol of solution is plotted against the mol fraction, N (abscissa). The tangent at the required point

is drawn. Its intercept on the ordinate $N_1 = 1$ is $\bar{G}_1$; that on the ordinate $N_2 = 1$ is $\bar{G}_2$.*

EXAMPLES.—1. The density of 39·19 per cent H_2SO_4 solution is 1·300 at 15°. Calculate: (a) the mol fraction of water, (b) the mol ratio of acid, (c) the molal vol. of the solution, and (d) the molality of the solution.

(a) The mol. wt. of $H_2SO_4 = 98$. The solution contains 39·19 g. of acid in 60·81 g. of water, or 39·19/98 = 0·4 mol of acid and 60·81/18 = 3·38 mols of water. Hence the mol fraction of water = 3·38/3·78 = 0·89. The mol fraction of acid = 0·11. (b) The mol ratio of acid = 0·11/0·89 = 0·124. (c) For 100 g. of solution = 77 c. c., $n_1 + n_2$ = 0·4 + 3·38 = 3·78. Hence vol. of solution for which $n_1 + n_2 = 1$ = molal vol. = 77/3·78 = 20·37 c. c. (d) 0·4 mols of H_2SO_4 are dissolved in 60·81 g. of water, so that the molality = 0·4 × 1000/60·81 = 6·578.

2. Calculate the differential heat of solution of H_2SO_4 in an aqueous solution of H_2SO_4 of mol fraction 0·5 from the following heats of solution of acid in water. ΔH is the heat absorbed per mol of solution (= heat absorbed per mol of acid × N_2, mol fraction of acid):

N_2	0·95	·85	·75	·65	·55	·45	·40	·35	·25	·15
$-\Delta H$ (cal.) ..	427	1207	1950	2639	3195	3456	3452	3378	2969	2125

The heat absorbed when 1 mol of a substance is dissolved in a solvent to form a given solution is the *total* or *integral heat of solution*, ΔH. The addition of a small amount of solute to a given solution causes a heat absorption per mol of solute called the *partial* or *differential heat of solution*, $\bar{H} = \partial(\Delta H)/\partial n$. In method (ii) above, ΔH is plotted against N_2 and the tangent at $N_2 = 0·5$ is drawn. This tangent intercepts the $N_1 = 1$ (or $N_2 = 0$) axis at -4820, which, therefore, is the value of $\partial(\Delta H)/\partial n_1 = \bar{H}_1$, the differential heat of solution of water in an acid solution of mol fraction 0·5. The intercept on the $N_2 = 1$ axis is -1900 cal., which is the required differential heat of solution.

In a similar way, the partial heat of solution of a solution of concentration $N_2 = 0·1$, say, in solution of concentration $N_2 = 0·5$, is measured by the intercept on the ordinate $N_2 = 0·1$ between the tangent at $N_2 = 0·5$ and the curve. It is -2940 cal.

3. The differential heat of solution (in cal.) of H_2SO_4 in a solution containing mol fraction N_2 of acid is:

$-\bar{H}_2$ ..	12,970	7520	4040	2960	1890	670	460	173	102	47
N_2 ..	0·1	·25	·40	·45	·50	·60	·65	·75	·80	·90

Calculate $\bar{H}_1$, the differential heat of solution of water in a solution containing a mol fraction 0·60 of acid. Compare the value with that obtained from the graph in the previous example.

From (6) it is seen that $\int d\bar{H}_1 = -\int N_2/N_1 \cdot d\bar{H}_2$. Hence plot the

* See Lewis and Randall, *Thermodynamics*, p. 36; Sosnick, *J. Amer. Chem. Soc.*, 1927, **49**, 2255.

values of N_2/N_1 against $\bar{H}_2$ (abscissa). Determine the area under the curve between $N_1 = 0$ and $N_1 = 0 \cdot 4$ (i.e. $N_2 = 0 \cdot 6$). Its negative value is the difference between the values of $\bar{H}_1$ for $N_1 = 0 \cdot 4$ and $N_1 = 0$. In default of the knowledge of $\bar{H}_1$ for $N_1 = 0$ the problem cannot be further solved. However, this value may be determined from the graph in Ex. 2; it is -8300 cal. The negative value of the area is $+2010$. Hence $\bar{H}_1 = 2010 - 8300 = -6290\ cal.$

CHAPTER I

Thermodynamics

(a) First Law of Thermodynamics

(1) The First Law (Law of Conservation of Energy).

Let Q be the heat *absorbed*, A the work *done*, by a system undergoing any change. Then

$$Q = A + \Delta U \quad \ldots \ldots \quad (7)$$

where ΔU is the *increase* in the *energy* (*intrinsic*, or *internal, energy*) of the system. If the change is a *cyclic process* (i.e. the system returns to its initial state) $\Delta U = 0$, since U depends only on the actual state of the system. A, Q, and U must be measured in the same units; otherwise $A = JQ$, where J is the *mechanical equivalent of heat*. If A is in ergs and Q in $15°$ gm. cal. (written cal. in this book), $J = 4 \cdot 184 \times 10^7$ (see table on p. 141).

(2) Expansion of Fluids.

The work performed by a liquid, gas, or solid which increases in volume by dv when it is subjected to uniform (*fluid*) pressure p is $dA = p\ dv$. In a finite expansion from v_1 to v_2, the work done is:

$$A = \int_{v_1}^{v_2} p\ dv. \quad (8)$$

A is positive (i.e. work is *done by* the system) when $dv > 0$, or $v_2 > v_1$; otherwise it is negative (i.e. work is *spent on* the system).

The integral in (8) can be evaluated if the relation between p and v, i.e. the *characteristic equation* of the fluid, is known (p. 40).

In the case of n mols of an *ideal gas* (p. 40) the relation is $pv = n\mathrm{R}T$ (equation 72), where T is the absolute temperature and R is a constant. Hence, for isothermal expansion,

$$A = \int_{v_1}^{v_2} p \, dv = n \int_{v_1}^{v_2} \mathrm{R}T \, dv/v = n\mathrm{R}T \ln v_2/v_1$$
$$= 2 \cdot 3026 \, n\mathrm{R}T \log v_2/v_1. \qquad . \quad (9)$$

If the expansion is adiabatic ($dQ = 0$) then $pv^\gamma = $ constant, where $\gamma = C_p/C_v$, the ratio of the molecular heats (C_v assumed constant), and the work per mol is

$$A = -\Delta U = (p_1v_1 - p_2v_2)/(\gamma - 1)$$
$$= \mathrm{R}(T_1 - T_2)/(\gamma - 1). \qquad . \quad . \quad (10)$$

Units.—If p and v are in atm. and l. respectively, A is in litre-atm. (l. atm.). In (9), v_2 and v_1 occur as a ratio and the unit of A depends on that of R, i.e. again on those of p and v. If A is required in l. atm., $\mathrm{R} = 0 \cdot 08207$ l. atm./mol. 1°.

The relation between p and v for liquids or solids is expressed in terms of the *coefficient of elasticity*, ε:

$$\varepsilon = 1/\eta = -v_0 \cdot dp/dv, \qquad . \quad . \quad . \quad (11)$$

where v_0 is the (initial) specific volume under a standard pressure at a given temperature; η ($=1/\varepsilon$) is the *coefficient of compressibility*. The value of dp/dv will depend on the conditions of compression (isothermal or adiabatic).

Units.—The dimensions of compressibility are [vol.]/[vol.] [pressure] = [pressure]$^{-1}$. The C.G.S. pressure unit used is the *megabar* ($= 10^6$ dynes/cm.^{2}); thus, the isothermal compressibility of Ag is $1 \cdot 01 \times 10^{-6}$ megabar^{-1}. This means that, for Ag at room temperature, $1 \cdot 01 \times 10^{-6} = -1/v_0 \cdot dv/dp$ or $dv = -1 \cdot 01 \times 10^{-6} v_0 \cdot dp$, so that $v = -1 \cdot 01 \times 10^{-6} v_0 p$, p being expressed in megabars, and v, v_0 in any (the same) arbitrary units.

(Compressibility in megabar^{-1}) $\times 81/80 =$ (compressibility in atm.$^{-1}$.)

EXAMPLES.—1. Calculate ΔU for the evaporation of 100 g. of water at 25° under a pressure of 750 mm., assuming water vapour an ideal gas. (Latent heat of evaporation $= 590$ cal./g. at 25° C.)

From (7) ΔU = heat absorbed − work done. The heat absorbed = $100 \times 590 = 59{,}000$ cal.; the work done = $p \cdot \Delta v$, since p is constant. If the vapour behaves as an ideal gas, 1 mol occupies 22·4 l. at S.T.P., and the vol. occupied by 100 g. at 750 mm. and 298° absolute = $100 \times 22\cdot4 \times 760 \times 298/18 \times 750 \times 273 = 137\cdot6$ l. But 100 g. of liquid occupies 0·1 l. approx.   Hence $\Delta v = 137\cdot5$ l. and the work done = $750 \times 137\cdot5/760$ l. atm. = 3284 cal.   ∴ $\Delta U = 59{,}000 - 3300 = 55{,}700$ cal., approx.

2. The law of expansion of a particular gas is $pv^{1\cdot2}$ = constant. Find the work done, in cal., when 1 l. at 10 atm. expands to a pressure of 1 atm.

The constant in the equation is $pv^{1\cdot2} = 10$. Hence the value of v corresponding to $p = 1$ atm. is $\sqrt[1\cdot2]{10} = 6\cdot813$. From (10), A = $(10 - 6\cdot813)/0\cdot2 = 15\cdot935$ l. atm. = 386 cal. The same result is obtained directly by the use of (8), taking $p = 10/v^{1\cdot2}$.

3. The isothermal compressibility coefficient of Ag is $1\cdot01 \times 10^{-6}$ megabar^{-1} at 20°. What is the vol. decrease of 1 kg. when the pressure is raised from 1 atm. to 1000 atm.? $(d = 10\cdot49$ at 20°; 1 atm. = 1,013,225 dynes/cm.^{2}.)

From the compressibility coefficient $\Delta v = -1\cdot01 \times 10^{-6}v_0 \, \Delta p$, where p is expressed in megabars. $\Delta p = 999$ atm. = $999 \times 1{,}013{,}225$ dynes/cm.^{2} = $999 \times 1{,}013{,}225/10^6$ megabars. Hence $\Delta v = -1\cdot01 \times 10^{-6} \times 999 \times 1{,}013{,}225/10\cdot49 \times 10^{-6}$ c. c./g. = $-9\cdot745 \times 10^{-5}$ c. c./g. = $-9\cdot745 \times 10^{-2}$ c. c./kg.

EXERCISES.—I

1. Fifty g. of N_2 at 0° and 2 atm. expand adiabatically to 0·2 atm. Calculate the final temperature and the work done in cal. ($\gamma = 1\cdot4$). [Hint.—Combine pv^{γ} = constant with pv = RT.]

2. Calculate the heat absorbed (in l. atm.) when 15 g. of O_2 at 18° C. are expanded isothermally from an initial pressure of 20 atm. to a final pressure of 1 atm.

3. The adiabatic compression of a mixture of $2H_2 + O_2$ from 377 c. c. to 30·7 c. c. caused explosion; the initial temperature was 20·5° and initial pressure 1 atm. Calculate the temperature of the explosion and the pressure at the moment of its occurrence ($\gamma = 1\cdot4$).

4. Fifty l. of air at 120° C. are expanded adiabatically until the pressure is halved. Calculate the vol. increase and the work performed in cal. What is the final temperature ($\gamma = 1\cdot4$)?

5. The isothermal compressibility of CCl_4 (liquid) is $89\cdot6 \times 10^{-6}$ megabar^{-1}. By how much do 10 l. of CCl_4 decrease in vol. when the pressure is raised from 1 atm. to 100 atm ($d = 1\cdot582$)?

6. Ten l. of an ideal gas at 25° are compressed adiabatically to 1 l. The final temperature is 1111° C. Calculate γ.

7. Calculate ΔU for the conversion of 10 l. of water vapour at 17·54 mm. and 20° into liquid at the same temperature and pressure. Latent heat of evaporation = 580 cal./g. at 20°.

8. Five l. of a perfect gas at 25° are expanded adiabatically to 6 l. at 5° C. Calculate C_p and C_v.

(b) SECOND LAW OF THERMODYNAMICS

The Second Law.

This may be written:

$$(Q_1 - Q_2)/Q_1 = (T_1 - T_2)/T_1 = N', \quad . \quad (12)$$

where Q_1, Q_2 are the amounts of heat absorbed and rejected at the absolute temperatures T_1 and T_2, respectively, in a *reversible cyclic* process. N' is the *efficiency* of the process. Since $Q_1 - Q_2 = A$ ($\Delta U = 0$ in a cycle) $A/Q_1 = (T_1 - T_2)/T_1$. When $T_1 - T_2$ is very small (dT), then

$$dA = Q \cdot dT/T, \quad . \quad . \quad . \quad (13)$$

where dA is the work obtained, and Q the heat absorbed at $T_1 = T$ (the higher temperature).*

EXAMPLE.—A mol of H_2 initially at 1 atm. and 75° C., used as the working substance in a reversible engine, is expanded isothermally to twice the initial vol. and then adiabatically to four times the initial vol. It is then compressed isothermally to a vol. such that a subsequent adiabatic compression causes it to return to its initial conditions. Calculate the work performed in each part of the cycle and find the efficiency of the process ($\gamma = 1.4$).
Let v be the initial vol.; initial $T = 348°$. Work in first part of cycle $= A_1 = 0.082 \times 348 \times 2.303 \log 2v/v = + 19.78 \, l. \, atm.$ To calculate A_2, the temperature after adiabatic compression, T_2, must be known: $348(2v)^{0.4} = T_2(4v)^{0.4}$ or $T_2 = 263.7°$. Hence $A_2 = 0.082 (348 - 263.7)/0.4 = + 17.28 \, l. \, atm.$ The gas is now isothermally compressed at $T_2 = 263.7$ to a vol. v'; $A_3 = .082 \times 263.7 \times 2.303 \log v'/4v$. Adiabatic compression from v' at $263.7°$ to v gives a final temperature of $348°$; hence $263.7(v')^{0.4} = 348(v)^{0.4}$, or $v'/v = 2.001$. Hence $A_3 = .082 \times 263.7 \times 2.303 \log 0.5 = - 14.99 \, l. \, atm.$ and $A_4 = 0.082 (263.7 - 348)/0.4 = - 17.28 \, l. \, atm.$ Efficiency $= (Q_1 - Q_2)/Q_1 = (19.78 - 14.99)/19.78 = 0.242.$ Note that by (12) the efficiency also equals $(T_1 - T_2)/T_1 = (348 - 263.7)/348 = 0.242.$

EXERCISES.—II

1. A reversible engine works between the temperatures of 185° C. and 37° C. Calculate the thermodynamic efficiency.

2. A mol of N_2 at 1 atm. and 0° C. is used as the working substance

* Throughout the present book absolute temperature is designated °K. In formulæ T refers to °K. and t to °C. Occasionally t is used for time. The principles applied in this chapter are discussed at length in Partington, *Chemical Thermodynamics*, 1924, referred to in the present book as *C. T.*

in a reversible engine. It is expanded isothermally to three times and then adiabatically to four times its original vol. It is then compressed isothermally to a certain vol. and finally adiabatically to its initial conditions. What is the efficiency of the process ($\gamma = 1 \cdot 4$)?

3. A Carnot's engine working between 350° C. and 50° C. does 8000 cal. of work per cycle. Find how much heat is supplied and rejected per cycle.

(c) THERMOCHEMISTRY

(i) Specific Heats.

(1) **Definitions.**—*The heat absorbed per g. of substance per unit rise in temperature* is the *true specific heat*, c, at a particular temperature. For m g. of the substance, the *heat capacity* is:

$$d\mathrm{Q}/d\mathrm{T} = mc. \quad \ldots \quad (14)$$

The value of $d\mathrm{Q}/d\mathrm{T}$ is indefinite unless the conditions of heating (e.g. $v = $ constant, or $p = $ constant) are specified. For a temperature rise T_1 to T_2,

$$\mathrm{Q} = m\int_{\mathrm{T}_1}^{\mathrm{T}_2} c\, d\mathrm{T}. \quad \ldots \quad (15)$$

This integral can be evaluated when c is known as a function of the temperature. It is found experimentally that the relationship $c = a + b\mathrm{T} + d\mathrm{T}^2$ is a fairly close approximation for most substances. Equation (15) may also be written

$$\mathrm{Q} = m\int_{\mathrm{T}_1}^{\mathrm{T}_2} c\, d\mathrm{T} = m\bar{c}(\mathrm{T}_2 - \mathrm{T}_1), \quad \ldots \quad (16)$$

where $\bar{c}$ is a constant, called the *mean specific heat* over the range of temperature $\mathrm{T}_2 - \mathrm{T}_1$. By putting $\mathrm{T}_1 = 0$ and $\mathrm{T}_2 = \mathrm{T}$ in (15) and (16) we get:

$$c = d(\bar{c}\mathrm{T})/d\mathrm{T}. \quad \ldots \quad (17)$$

The distinction between c and $\bar{c}$ is most important; in elementary physics they are usually confused. The specific heats at *constant volume* (c_v) and at *constant pressure* (c_p) are defined, per g. of substance, by (*C. T.*, § 12):

$$c_v \equiv (d\mathrm{Q}/d\mathrm{T})_v = (d\mathrm{U}/d\mathrm{T})_v, \quad \ldots \quad (18)$$

$$c_p \equiv (d\mathrm{Q}/d\mathrm{T})_p = c_v + l_v(dv/d\mathrm{T})_p. \quad \ldots \quad (19)$$

The corresponding molecular heats ~~~~~ ~~~~~ ~~~~~ and $Mc_p = C_p$.

For unit mass l_v in (19) is the *latent heat of expansion* $(dQ/dv)_T$, i.e. the heat absorbed per c. c. increase in volume at constant temperature. It is given by *Clapeyron's equation* (*C. T.*, § 29):

$$l_v = T(dp/dT)_v, \quad \cdots \cdots (20)$$

in which $(dp/dT)_v$ is the pressure increase per degree rise in temperature at constant volume. If $(dp/dT)_v$ is in (dynes/cm.²)/1° C., l_v is in ergs.

The difference between c_p and c_v is (equations 21–5)

$$c_p - c_v = T(\partial v/\partial T)_p (\partial p/\partial T)_v = - T(\partial v/\partial T)_p{}^2/(\partial v/\partial p)_T$$
$$= - T(\partial v/\partial T)_p{}^2 (\partial p/\partial v)_T = T\alpha^2 v_0/\eta_T = T\alpha^2/\eta_T d,$$

where $\alpha = (\partial v/\partial T)_p/v_0 =$ coefficient of expansion, η_T is the isothermal compressibility (p. 7), and $d = 1/v_0$ is the density at 0° C. (*C. T.* § 30). Values of $(\partial v/\partial T)_p$ and $(\partial v/\partial p)_T$ may be obtained by differentiation of the characteristic equation.

EXAMPLES.—1. The true specific heat of Pb ($d = 11\cdot37$) at $t°$ C. is $c = 0\cdot0297 + 0\cdot0_4 1358t$. Calculate the mean specific heat over the range 0° to 100°. What is the heat absorbed when 10 g. of Pb are heated from 15° to 120°? If the coefficient of cubical expansion of Pb is $82\cdot8 \times 10^{-6}$ per degree, calculate the ratio of the heat absorbed to the external work.

Use (16): $100\bar{c} = \int_0^{100} (0\cdot0297 + 0\cdot0_4 1358t)\,dt = [0\cdot0297t + 0\cdot0_5 679t^2]_0^{100} = 3\cdot04$, whence $\bar{c} = 0\cdot0304$. The heat absorbed, Q, $= m \int_{t_1}^{t_2} c\,dt = 10[0\cdot0297t + 0\cdot0_5 679t^2]_{15}^{120} = 32\cdot16$ g. cal. or $32\cdot16 \times 4\cdot184 \times 10^7$ ergs $= 134\cdot6 \times 10^7$ ergs. Also $\alpha = 1/v_0(dv/dT)_p = 82\cdot8 \times 10^{-6}$ ∴ $dv = 82\cdot8 \times 10^{-6}\,dT/11\cdot37 = 7\cdot283 \times 10^{-6} \times 105 = 0\cdot0007644$ c. c./g. Hence, vol. increase of 10 g. $= 0\cdot007644$ c. c. and the work ($p =$ constant $= 1$ atm.) $= 0\cdot007644$ c. c. atm. $= 7644 \times 1\cdot01325$ ergs. The required ratio is $134\cdot6 \times 10^7/7644 \times 1\cdot01325 = 17\cdot38 \times 10^4$.

2. The adiabatic compressibility of C_6H_6, η_Q, at 20° C. is $66\cdot25 \times 10^{-6}$ atm.$^{-1}$, the isothermal value being $95\cdot3 \times 10^{-6}$. If c_p (1 atm.) $= 0\cdot4084$, find c_v. If α, the coefficient of expansion, is $0\cdot00124$ per degree and $d = 0\cdot879$ (both at 20°), find $(\partial u/\partial v)_T$ in g. cal./c. c./g. According to *Reech's theorem* (*C. T.*, p. 23):

$$\varepsilon_Q/\varepsilon_T = c_p/c_v = \eta_T/\eta_Q. \quad \cdots \cdots (26)$$

Hence $c_v = 0.4084 \times 66.25 \times 10^{-6}/95.3 \times 10^{-6} =$ *cal./g.* To answer the second part calculate l_v by (19) and then use

$$(\partial u/\partial v)_{\text{T}} = l_v - \jmath \qquad (27)$$

Now $\alpha = (\partial v/\partial \text{T})_p / v_0 = 0.00124$ per $1°$; $\therefore$ $(\partial v/\partial \text{T})_p = 0.00124$ $/0.879$ c. c./$1° = 0.001411$ c. c./$1°$. Hence $l_v = (c_p - c_v)/(\partial v/\partial \text{T})_p$ $= 0.1245/0.001411 = 88.23$ cal./c. c. In order to use (27) p must be in the same units as l_v; i.e. g. cal./c. c. Now, $p = 1$ atm. $= 1,013,225$ dynes/cm.$^2 = 1,013,225$ ergs/cm.$^3 = 1,013,225 \times 0.239$ $\times 10^7$ cal. / cm.$^3 = 0.02421$ cal. / cm.^{3} Hence $(\partial u / \partial v)_{\text{T}} = 88.23$ $- 0.02421$ cal./c. c. $= 88.2$ *cal./c. c.* This result refers to 1 g., since c_p, c_v, and v_0 have been referred to 1 g.

EXERCISES.—III

1. The true specific heat of Co is $c = 0.10584 + 0.0_4457334t$ $+ 0.0_7658281t^2$ between $0°$ and $890°$ Calculate the mean specific heat over this temperature range.

2. The true specific heat of Fe at $100°$ C. is 0.1124; the mean specific heat over the range $0°$ to $100°$ C. is 0.1089. Find a linear relation between the true specific heat and the temperature.

3. The mean specific heat of Al over the range t_1 to t_2 is given by $\bar{c}$ $= 0.222 + 0.0_45 \, (t_1 + t_2)$, provided t_2 is below $600°$. What is the true specific heat at $0°$ C.?

4. The following values give the mean specific heat of Pt: $-186°$ to $-79°, \bar{c} = 0.0277$; $-79°$ to $18°$, $\bar{c} = 0.0311$; $18°$ to $100°$, $\bar{c} = 0.0324$. Show that the true specific heat of Pt is $c = 0.03108 + 0.0_41004t +$ 0.0_818t^2.

5. The mean specific heats of Ge are: $0°$ to $100°$, 0.0735; $0°$ to $211°$, 0.0774; $0°$ to $300°$, 0.0768. What is the true specific heat at $250°$?

6. The specific volume of mercury is given by: $v = v_0 [1 + 0.018161t$ $/100 + 0.0_478 \, (t/100)^2]$ at $t°$ C. The specific heat at 1 atm. is given by $0.033458 - 0.0_41074t + 0.0_7385t^2$, and the density at $0°$ C. is 13.5955. Find the specific heat at $25°$ C. under 100 atm. pressure if

7. If ε_Q for C_6H_6 is 66.25×10^{-6} atm. at $20°$, ε_{T} is 95.3×10^{-6} atm., and c_p is 0.4084, calculate c_v.

8. Calculate $c_p - c_v$ for Hg, for which $d = 13.546$ at $20°$; $\alpha \times 10^{10}$ $= 1,805,553 + 12,444(t/100) + 2539(t/100)^2$ (where $t = °$C.), and $\eta_{\text{T}} = 3.8 \times 10^{-6}$ (kg./cm.^{2})$^{-1}$.

9. For potassium, $\eta_{\text{T}} = 33.0 \times 10^{-6}$ atm.$^{-1}$ and $\alpha = 25 \times 10^{-5}$ per $1°$. If $d = 0.8598$ at $20°$, calculate $c_p - c_v$ at $20°$.

10. The coefficient of cubical expansion of Cu is 59.8×10^{-6} per $1°$ between $0°$ and $300°$. Calculate the ratio of the external work to the heat absorbed when 4 kg. of Cu ($d = 8.93$; $c = 0.10079 + 0.0_561t$) are heated from $0°$ to $300°$ C.

11. The specific volume of Ag is represented by $v = 0.0952 \, (1 +$

$0.0_45246t + 0.0_5405t^2$). Between 0° and 100° the true specific heat is given by $0.0556 (1 + 0.0003396t - 0.0_6141t^2)$. What is the ratio of the heat absorbed to the external work done when 1 kg. of Ag is heated from 0° to 100°?

12. Using the equation

$$\eta_T - \eta_Q = T(\partial v/\partial T)_p{}^2 d/c_p, \quad . \quad . \quad . \quad (28)$$

where d is the density, calculate c_p and c_v for EtOH at 80°, given that η_T and η_Q are 171×10^{-6} atm.$^{-1}$ and 144.3×10^{-6} atm.$^{-1}$, that the specific volume, v, is 1.3609, and $dv/dT = 0.00181$ c. c./1°.

13. The atomic heats at constant pressure and constant volume for a substance are related empirically as follows:

$$C_p - C_v = aTC_p{}^2 = k'T^{3/2}, \quad . \quad . \quad . \quad (29)$$

where k' is a constant characteristic of each substance and $a = 0.0214/T_s$, T_s being the m. p.

Calculate c_v for Pt at 20° C., given that $\eta = 0.21 \times 10^{-6}$ megabar^{-1}, $\alpha = 2.66 \times 10^{-5}$ per 1°, and v, the specific volume, $= 0.0478$ at 20°; m. p. $= 1710°$ C.

14. The specific volume of H_2O, v, is 1.00177 at 20°; $dv/dT = 0.0_3207$; $\eta_T = 45.9 \times 10^{-6}$ atm.$^{-1}$ and $\eta_Q = 45.6 \times 10^{-6}$ atm.$^{-1}$. Calculate the latent heat of expansion at 20°.

15. Calculate c_v for the following substances at the temperatures given; α is the coefficient of cubical expansion (T^{-1}), η_T is the isothermal compressibility coefficient (megabar^{-1}), and d is the density.

		$\alpha \times 10^6$	$\eta_T \times 10^6$	c_p	d	T
(i)	Al ..	23	1.3	0.2096	2.70	273
(ii)	Fe ..	10	0.4	0.1045	7.86	273
(iii)	Cu ..	16	0.54	0.0909	8.93	273
(iv)	I_2 ..	84	13.0	0.0540	4.95	288
(v)	Pb ..	29	2.2	0.0302	11.37	273

16. According to Berthelot's equation of state for gases,

$$C_p - C_v = R(1 + 27p\,T_c^3/16p_c T^3), \quad . \quad . (29a)$$

where $R = 1.9875$ cal./mol, and p_c, T_c are the critical pressure and temperature. For CO_2, $\gamma = 1.302$ at 15° and 1 atm.; $p_c = 73$ atm. and $T_c = 31.1°$ C. Calculate C_p and C_v.

(2) **Quantum Theory of Specific Heats.**—According to the quantum hypothesis a resonator may absorb or emit energy only in whole multiples of a quantum of energy, ε. If ν is the frequency of the resonator, then

$$\varepsilon = h\nu, \quad . \quad . \quad . \quad . \quad . \quad (30)$$

where h is a universal const. ($= 6\cdot560 \times 10^{-27}$ erg. sec.). Among the formulæ available for calculating ν for a solid are the following:

(a) Einstein: $\qquad \nu = 2\cdot8 \times 10^7/A^{\frac{1}{3}} \eta^{\frac{1}{2}} d^{\frac{1}{6}}, \qquad . \quad . \quad .$ (31)

where A is the atomic weight, η the compressibility, and d the density. (See Ex. 4 for units.)

(b) Lindemann: $\qquad \nu = 2\cdot8 \times 10^{12}\sqrt{T_s/Av^{\frac{2}{3}}}, \quad . \quad . \quad .$ (32)

where T_s is the m.p. and v the atomic volume. In the case of binary compounds, $A = 0\cdot5 \times$ (mol. wt.).

The following formulæ have been proposed for the atomic heats ($=$ sp. ht. $\times$ at. wt.) of isotropic crystalline solids on the basis of the quantum hypothesis:

(i) Einstein (1907): $\quad C_v = 3Rx^2[e^x/(e^x - 1)^2]. \qquad . \quad .$ (33)

(ii) Nernst and Lindemann (1911):

$$C_v = \frac{3R}{2}\left[x^2 \frac{e^x}{(e^x - 1)^2} + \left(\frac{x}{2}\right)^2 \frac{e^{x/2}}{(e^{x/2} - 1)^2} \right]. \quad (34)$$

(iii) Debye (1912):

$$C_v = 3R\left[\frac{4\pi^4}{5x^3} - \frac{3x}{e^x - 1} \right.$$
$$\left. - 12x \sum_{n=1}^{n=\infty} e^{-nx}\left\{ \frac{1}{nx} + \frac{3}{n^2x^2} + \frac{6}{n^3x^3} + \frac{6}{n^4x^4} \right\} \right], \quad (35)$$

which may also be written, when $x < 2$:

$$C_v = 3R[1 - x^2/20 + x^4/560 - x^6/18{,}144 + x^8/633{,}600$$
$$- x^{10}/23{,}063{,}040 + \ldots]. \quad . \quad . \quad . \quad . \quad (35a)$$

In these equations R is the gas constant (cal./1°); $x = \beta\nu/T$ where $\beta = h/k$ and $k = R/N_0 = 1\cdot37 \times 10^{-16}$ erg./1°, N_0 being the Avogadro constant ($6\cdot059 \times 10^{23}$); e^x is the exponential function. Since $C_v = dU/dT$, (35) can be integrated:

$$U = \frac{9RT}{12}\left(\frac{C_v}{3R} + \frac{3x}{e^x - 1} \right) =$$
$$\tfrac{3}{4}RT\left(\frac{77\cdot94}{x^3} - 12x \sum_{n=1}^{n=\infty} e^{-nx}\left\{ \frac{1}{nx} + \frac{3}{n^2x^2} + \frac{6}{n^3x^3} + \frac{6}{n^4x^4} \right\} \right). \quad (36)$$

Analogous expressions may be obtained from the other functions.

Equation (35) may be written in the form $C_v = f(T/\theta)$, where $\theta (= \beta v)$ is the *characteristic temperature* of the substance.* At very low temperatures the equation becomes

$$C_v = a(T/\theta)^3 = constant \times T^3, \quad . \quad . \quad (37)$$

where a is a universal constant ($= 77.938 \times 3R$).

According to Nernst, the mol. heat of a binary molecule, $2C_v$, is given by

$$2C_v = D(\beta v_1/T) + E(\beta v_2/T), \quad . \quad . \quad (38)$$

where D represents the Debye function (35) and E the Einstein function (33). v_1 is determined by (32) and v_2 by the "Residual Ray" method (see *C. T.*, pp. 249, 253). Equation (34) holds for some solids, e.g. KCl.

The functions $E(\theta/T)$, $N(\theta/T)$, and $D(\theta/T)$ have been tabulated for values of θ/T.† The following table gives $f(\theta/T)$, where $3Rf(\theta/T) = D(\theta/T)$, for values of T/θ: ‡

T/θ	$f(\theta/T)$	T/θ	$f(\theta/T)$	T/θ	$f(\theta/T)$
∞	1·000	0·8	0·926	0·20	0·369
4	0·997	0·7	0·904	0·15	0·213
3	0·994	0·6	0·872	0·10	0·0758
2	0·988	0·5	0·825	0·075	0·0328
1·5	0·978	0·4	0·745	0·050	0·00974
1·0	0·952	0·3	0·607	0·025	0·00122
0·9	0·941	0·25	0·503	0·000	0·000

By plotting these figures on squared paper a curve can be drawn which will enable intermediate values to be interpolated.

EXAMPLES.—1. Calculate the atomic heat of Al at 86° K. by means of Debye's expression, given that $\beta v = 398$.

The equation is (35); $x = \beta v/T = 398/86 = 4.628$. Hence $4\pi^4 x^{-3}/5$

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* The characteristic temperature used by G. N. Lewis is the temperature at which $C_v = 3R/2$. It is equal to $\beta v/4.02$. According to Krase (1922) $f(T/\theta) = 2.91 + 2.89 \tanh(2.95 \log T/\theta)$; this affords another simple method of using Debye's equation.

† See Nernst, *The New Heat Theorem*, Eng. Tr., 1926, p. 246.

‡ Jeans, *Dynamical Theory of Gases*, 2nd Ed., p. 424. Values of e^x are tabulated in *H. M.*, p. 266.

$= 0.786157$. Also $3x / e^x - 1 = 3 \times 4.628 / 101.309 = 0.137046$.
Omitting the $12x$, the last term is evaluated as follows. Let $y = e^{-x} = e^{-4.628} = 0.00977429$; then:

$$\sum_{n=1}^{n=\infty} y^n \cdot (nx)^{-1} = \frac{1}{x} \left\{ y + \frac{y^2}{2} + \frac{y^3}{3} + \dots \right\} = 0.0021224$$

$$\sum_{n=1}^{n=\infty} y^n \cdot 3(nx)^{-2} = \frac{3}{x^2} \left\{ y + \frac{y^2}{2^2} + \frac{y^3}{3^2} + \dots \right\} = 0.0013724$$

$$\sum_{n=1}^{n=\infty} y^n \cdot 6(nx)^{-3} = \frac{6}{x^3} \left\{ y + \frac{y^2}{2^3} + \frac{y^3}{3^3} + \dots \right\} = 0.0005924$$

$$\sum_{n=1}^{n=\infty} y^n \cdot 6(nx)^{-4} = \frac{6}{x^4} \left\{ y + \frac{y^2}{2^4} + \frac{y^3}{3^4} + \dots \right\} = 0.0001279$$

$$\text{Total} \quad = \overline{0.0042151}$$

But $12x \times 0.0042151 = 12 \times 4.628 \times 0.0042151 = 0.23410$.   Hence $C_v = 3 \times 1.9875 \,(0.786157 - 0.137046 - 0.23410) = 3 \times 1.9875 \times 0.415011 = 2.4745$.   The observed value for Al is $C_p = 2.52$. The calculated C_v must be converted to C_p in order that a comparison may be made.   A calculation with the aid of Reech's Theorem shows that $C_p/C_v = 1.042$.   Hence C_p (calculated) $= 2.58$.

2. Calculate the atomic heat of Cu at $86°$ K. using Einstein's formula; $\beta v = 240$ and $C_p/C_v = 1.025$.
In this case $x = \beta v/T = 240/86 = 2.79$, $e^x = 16.281$, and hence $C_v = 3 \times 1.985 \times (2.79)^2 \times 16.281/(15.281)^2 = 3.23$, or $C_p = 3.23 \times 1.025 = 3.31$. The observed value is 3.38.

3. Calculate the molecular heat of KCl at $235°$ K. with the aid of the Nernst-Lindemann equation, given that $c_p/c_v = 1.038$ and $\beta v = 218$.
We have $x = \beta v/T = 218/235 = 0.9276$, and $e^x = 2.5285$. Hence $x^2 e^x/(e^x - 1)^2 = (0.9276)^2 \,(2.5285) / (1.5285)^2 = 0.9383$; also $x^2 e^{x/2}/4(e^{x/2} - 1)^2 = (0.9276)^2 (1.5901) / 4(0.5901)^2 = 0.98245$. Hence C_p (mol.) $= 2 \times 1.038 \times 1.5 \times 1.985 \,(0.9383 + 0.98245) = 11.87$. The observed value is 11.78.

4. Calculate the atomic frequency for Al, given $\eta = 1.3 \times 10^{-6}$ megabar^{-1}; $d = 2.70$.
Use (31). $\eta = 1.3 \times 10^{-6}$ megabar$^{-1} = 1.3 \times 10^{-12}$ cm.^{2}/dyne, and $\eta^{\frac{1}{2}} = 1.14 \times 10^{-6}$. Also $d = 2.70$ and $d^{\frac{1}{3}} = 1.18$; A$^{\frac{1}{3}} = (27)^{\frac{1}{3}} = 3$. Hence $v = 2.8 \times 10^7/3 \times 1.14 \times 10^{-6} \times 1.18 = 6.8 \times 10^{12}$.

<div align="center">EXERCISES—IV</div>

1. Calculate the atomic heats of the following substances by the equations mentioned:

    (i) Ag at $270°$ K. by (33); $\beta v = 215$.
    (ii) Al at $137°$ K. by (35); $\beta v = 398$.
    (iii) Cu at $323°$ K. by (34); $\beta v = 321$.
    (iv) Pb at $200°$ K. by (34); $\beta v = 95$.
    (v) Diamond at $262°$ K. by (35); $\beta v = 1860$.

2. Calculate the atomic heat of Pb (at constant pressure) at 17° C., using (34); $\beta\nu = 95$ and a in (29) is $3\cdot0 \times 10^{-5}$.

3. Assuming the m.p. of diamond ($d = 3\cdot3$) to be 3600° C. calculate with the aid of (32) and (34) the specific heat, c_v, of this substance at 232° K.

4. Calculate C_v for KCl at 143° C., using (38), if $\beta\nu_1 = 166$ and $\beta\nu_2 = 213\cdot5$.

5. Calculate C_v for AgCl at 87° K., using (38); $\beta\nu_1 = 102$, $\beta\nu_2 = 179$.

6. The ratio of the atomic heats for Ag, C_p/C_v, is $1\cdot047$. Calculate C_p at 535° K., using Debye's equation, given that $\beta\nu = 215$. Compare this value with that obtained by the Nernst-Lindemann equation.

7. Calculate the atomic frequency of Ag, given that its melting-point is 1234° K. and its atomic volume $10\cdot3$.

(ii) Latent Heats.

(1) Clapeyron-Clausius Equation.—According to this,

$$L = T\Delta v \,.\, dp/dT. \quad \ldots \quad (39)$$

L is the latent heat of transition of 1 g. of substance at T° K., $\Delta v = v_2 - v_1$, where v_1, v_2 are the specific volumes of the disappearing phase and the phase produced, respectively. The equation is exact apart from the slight variation of Δv with pressure. It applies to systems in which the pressure depends only on the temperature and not on the volume, and therefore to fusion, evaporation, sublimation, and some cases of chemical change (dissociation).

Units.—If Δv is in cm.^{3}/g. and dp/dT in atm./1°, then L is in atm. $\times$ cm.^{3}/g. (1 cal. $= 41\cdot29$ atm. $\times$ cm.^{3}). If dp/dT is expressed in (dynes/cm.^{2})/1°, Δv still being in cm.^{3}/g., then L is obtained in ergs/g. (1 cal. $= 4\cdot184 \times 10^7$ ergs).

(2) **Fusion.**—Equation (39) holds exactly, v_2 referring to the liquid and v_1 to the solid phase under the actual pressure of the experiment. *No simplifying assumptions are permissible.* Δv may be positive or negative and accordingly the m.p. is raised (sulphur) or depressed (ice) by increase of pressure. The value of L_f per mol, ML_f, is denoted by λ_f.

EXAMPLE.—The freezing-point of C_6H_6 is $5\cdot40°$ and $v_l - v_s$ at this temperature is $13\cdot01 \times 10^{-3}$ c.c./g., v_l and v_s being the specific volumes of the liquid and solid, respectively. Calculate the change in melting-point under a pressure of 100 atm. Use (39). $L_f = 30\cdot6 \times 4\cdot2 \times 10^7$ ergs/g.; T $= 273 + 5\cdot4 = 278\cdot4°$; $\Delta v = 13\cdot01 \times 10^{-3}$ c.c./g. Hence $dT/dp = 278\cdot4 \times 13\cdot01 \times 10^{-3} / 30\cdot6 \times 4\cdot2 \times 10^7$ degrees / (dynes / cm.^{2}) $= 278\cdot4 \times 13\cdot01$

$\times 10^{-3} \times 1{,}013{,}225/30\cdot6 \times 4\cdot2 \times 10^{7}$ degrees/atm. $= 0\cdot002854°$ per atm. But $dp = 100 - 1 = 99$ atm.; $\therefore dT = 99 \times 0\cdot002854 = 0\cdot283°$. Hence m.p. rises to $5\cdot40 + 0\cdot283 = 5\cdot683°$.

EXERCISES.—V

1. The densities of solid and liquid Bi at the m.p., $271°$, are $9\cdot637$ and $10\cdot005$ g./c.c. respectively. If λf is 2600 g. cal., under what pressure will Bi melt at $270\cdot8°$?

2. The m.p. of naphthalene is related to the pressure, p (atm.), by the equation t (°C.) $= 79\cdot8 + 0\cdot0373p + 0\cdot0_519p^{2}$. If $v_l - v_s = +0\cdot146$ c.c./g. (independent of p), calculate Lf at the m.p. under 50 atm. pressure.

3. The m.p. of Sn, $t°$ C., under a pressure of p atm. is given by $t = 231\cdot8 + 0\cdot0033\ (p - 1)$. The heat of fusion is $14\cdot05$ cal./g. If the density of the liquid at 1 atm. is $6\cdot988$, calculate that of the solid.

4. The density of water at $0°$ C. is $0\cdot99987$ and the density of ice at the same temperature is $0\cdot91670$, whilst the latent heat of fusion of ice is 80 cal./g. Calculate the f.p. of water under a pressure of 5 atm. (Lond. B.Sc. Hons., 1922).

5. Using the following equation of state for O_2: $p = 2\cdot564T/(v - \delta) - 1475/(v + 0\cdot09)^{2}$ where $\log \delta = 0\cdot1420 - 0\cdot303/v$, p being in atm. and v in c.c./g., calculate the heat of union of Ag with O_2 to form Ag_2O at $500°$. The equilibrium pressure of O_2 over Ag_2O is given by $\log p = -2859/T + 6\cdot2853$, and the density of Ag_2O is $7\cdot5$ and that of Ag $10\cdot5$. (Hint: The reversible formation of Ag_2O from Ag and O_2 may be regarded as a physical transition with regard to O_2.)

(3) **Evaporation.**—Equation (39) holds. The molecular heat of *evaporation*, λ_e ($= ML_e$), is given by

$$\lambda_e = T(V_2 - V_1) \cdot dp/dT, \quad . \quad . \quad (40)$$

where $V_2 = Mv_2$ (vapour) and $V_1 = Mv_1$ (liquid). If we neglect V_1 in comparison with V_2 and assume that the saturated vapour obeys the gas laws (which is approximately true at low temperatures, i.e. low vapour pressures) we have $V_2 = RT/p$ and therefore

$$1/p \cdot dp/dT = d \ln p/dT = \lambda_e/RT^{2}. \quad (41)$$

Units.—The unit in which p is expressed is immaterial, since $d \ln p/dT$ involves only the *ratio* of the pressures. λ_e is obtained in the same units as RT; if R is expressed in (cals./mol)/1°($= 1\cdot9875$ g. cal./1° C.), then λ_e is obtained in l./mol

The integration of (41) on *the assumption that λ_e is independent of* T gives:

$$\ln p = -\lambda_e/RT + constant, \qquad . \quad . \quad (42)$$

or

$$\lambda_e = \frac{RT_2 T_1}{T_2 - T_1} \ln \frac{p_2}{p_1} = 4 \cdot 576 \frac{T_2 T_1}{T_2 - T_1} \log \frac{p_2}{p_1} \text{ cal.} \quad . \quad (42a)$$

Vapour-pressure Equations.—(i) The integration of (41) on the assumption that $\lambda_e = \lambda_0 + aT$ (where $a =$ constant) gives Kirchhoff's vapour-pressure equation:

$$\ln p = -\lambda_0/RT + a(\ln T)/R + constant, \qquad (43)$$

or

$$\log p = A/T + B \log T + C. \quad . \quad . \quad . \quad . \quad (43a)$$

(ii) Van der Waals' vapour-pressure equation is

$$\log p_c/p = a(T_c/T - 1), \quad . \quad . \quad . \quad (44)$$

where p_c is the critical pressure and T_c the critical temperature; $a = f(T)$, but is very nearly constant (approx. $3 \cdot 0$).

(iii) Bertrand's vapour-pressure equation is

$$p = A[(T - B)/T]^n, \quad . \quad . \quad . \quad (45)$$

where A, B, and n are constants; $n = 50$ approx.

Ramsay and Young's rule states that if p, p' are the vapour pressures of a substance A at T_A, T_A', and of a substance B at T_B, T_B', then

$$T_A'/T_B' = T_A/T_B + c(T_A' - T_A), \qquad . \quad (46)$$

where c is a small constant. When the substances are chemically similar (e.g. esters) $c = 0$, and (46) becomes *Dühring's rule*:

$$T_A'/T_B' = T_A/T_B, \quad . \quad . \quad . \quad (47)$$

or

$$(T_A' - T_A)/(T_B' - T_B) = T_A/T_B = constant. \quad (47a)$$

It holds accurately for unsaturated salt solutions with water as a reference liquid.

(4) **Sublimation.**—Equations (40) to (43a) apply for λ_s, v_1 being the vol. of the solid.

(5) **Dissociation.**—Equation (39) applies when p depends

only on T. When n mols of vapour are formed from 1 mol solid, $V_2 = nRT/p$, and the expression for λ_d is n times that for λ_e in (41) to (42a).

The *heat of hydration* of a salt by *liquid* water is given by the equation

$$Q = n\,RT^2\,d(\ln p_0/p)/dT, \quad . \quad . \quad . \quad (48)$$

where n is the number of mols of water attaching themselves to each mol of salt, p is the dissociation pressure of the higher hydrate, and p_0 the vapour pressure of water at T. Integration of (48) on the assumption that Q is independent of T gives

$$n \log \frac{(p_0/p)_2}{(p_0/p)_1} = \frac{Q}{4\cdot576} \cdot \frac{T_2 - T_1}{T_2 T_1}, \qquad . \quad (48a)$$

Q being the heat *absorbed* in cal. per mol of salt.

EXAMPLES.—1. The density of C_6H_5Cl at the b.p., $132°$, is $0\cdot9814$ g./c.c. for the liquid and $0\cdot00359$ g./c.c. for the saturated vapour. If dp/dT for this temperature is $20\cdot5$ mm./$1°$, calculate the heat of evaporation at the b.p. Compare this value with that obtained by assuming the gas laws.

Use (39). $\Delta v = v_g - v_l = (1/0\cdot00359) - (1/0\cdot9814) = 278\cdot6$ $- 1\cdot019 = 277\cdot6$ c.c./g. Also $T = 273 + 132 = 405°$ K. and dp/dT $= 20\cdot5/760$ atm./$1° = 20\cdot5 \times 1,013,225/760$ (dynes/cm.²)/$1°$. Hence $L_e = 405 \times 277\cdot6 \times 20\cdot5 \times 1,013,225/760 = 3\cdot073 \times 10^9$ ergs $= 3\cdot073 \times 10^9/4\cdot184 \times 10^7$ cal. $= 73\cdot43$ *cal./g.*

Equation (41) entails assumption of the gas laws; the vol. of the liquid is neglected. At the b.p. $p = 760$ mm.; hence $1/p \cdot dp/dT$ $= d \ln p/dT = 1/760 \cdot 20\cdot5 = 0\cdot026975/1°$; $R = 1\cdot99$ (cal./mol)/$1°$. Thus $\lambda_e = 0\cdot026975 \times 1\cdot99 \times (405)^2 = 8808$ cal./mol; $L_e = 8808/112\cdot5$ $= 78\cdot3$ *cal./g.* The two results differ by $6\cdot6$ per cent, which represents the error due to the approximations used in the second calculation.

2. The heat of evaporation of water, L_e, is 539 cal./g. at the b.p. under 760 mm. Under what pressure will water boil at $98°$?

Using (41) we find dp/dT, which is the relationship between pressure increase and temperature increase. $dT = 98° - 100° = - 2°$; also $\lambda_e = 539 \times 18$. Hence $d \ln p/dT = \lambda_e/RT^2 = 539 \times 18/1\cdot99(373)^2$ $= 0\cdot03504 = 1/p \cdot dp/dT$. Put $p = 760$ mm.; then $dp/dT = 760$ $\times 0\cdot03504 = 26\cdot63$ mm./$1°$ at $373°$ K. Hence $dp = 26\cdot63 dT$ $= -26\cdot63 \times 2$ mm. $= -53\cdot26$ mm. The required pressure is $760 - 53 = 707$ *mm.* (Obs. 707·27.)

3. Calculate λ_e for Ca from the following vapour pressures on the assumption that λ_e is independent of T:

p (mm.) ..	4	6	23	41	49	99	287
t (°C.) ..	960	988	1021	1039	1079	1092	1107

Find also the b.p. of the metal, T_s.

From (41) we have $(1 \cdot 985 \times 2 \cdot 303/\lambda_e) \cdot d \log p = d\mathrm{T}/\mathrm{T}^2 = - d(1/\mathrm{T})$. Hence $\log p = k \cdot 1/\mathrm{T} + \mathrm{C}$, where $k = - \lambda_e/1 \cdot 985 \times 2 \cdot 303$. Plot $\log p$ against $1/\mathrm{T}$; the slope of the straight line so drawn that the experimental points are distributed evenly about either side is k (fig. 1; p in atm.). By counting the squares the slope is seen to be $- 4 \cdot 75$ ordinate units$/5 \cdot 85$ abscissa units $= - 4 \cdot 75 \times 0 \cdot 5/5 \cdot 85 \times$
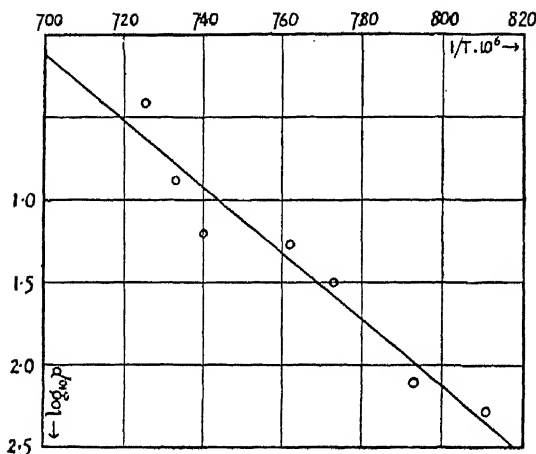
Fig. 1.—Vapour Pressure of Calcium

$20 \times 10^{-6} = - \lambda_e/1 \cdot 985 \times 2 \cdot 303$; or $\lambda_e = 92{,}800$ cal. By extrapolation to $\log p = 0$ (i.e. $p = 1$ atm.) $1/\mathrm{T}_s$ is seen to be 694×10^{-6}, whence $\mathrm{T}_s = 1167°$ K.

4. The b.p. of C_2H_5OH under different pressures is:

p (mm.) ..	12·0	17·0	23·5	43·8	78·6	134·9	198·1
b.p. (°C.) ..	0	5	10	20	30	40	47·7

The density of C_2H_5OH is $0 \cdot 7894$ g./c.c.; that of its saturated vapour is $0 \cdot 000111$ g./c.c., both referring to $20°$. Calculate the latent heat of evaporation per g. of C_2H_5OH at $20°$.

First obtain $dp/d\mathrm{T}$ at $20°$. Plot p against T (fig. 2) and draw a straight line through those points on the curve corresponding with $t = 20 \cdot 5°$ and $t = 19 \cdot 5°$. This line will be a very close approximation to the tangent * to the curve at $20°$ C. By counting up the squares we find for the slope of the line AB/BC $= 4 \cdot 9$ divisions$/3 \cdot 6$ divisions. But 1 division on ordinate $= 20/760$ atm., and 1 division on abscissa $= 10°$. Hence $dp/d\mathrm{T} = 4 \cdot 9 \times (20/760)/3 \cdot 6 \times 10 = 0 \cdot 00306$ atm./1°. On applying (39) we have $(1/0 \cdot 000111 = 9010$ c.c./g.; $1/0 \cdot 7894 =$

* The position of the tangent at any point on a given curve is readily determined by means of a simple " tangentimeter ". See Latshaw, $\mathcal{J}$. Amer. Chem. Soc., 1925, 47, 793.

$$L_e = 293 \times 0.00306 \times (1{,}013{,}225 / 4.18 \times 10^7) \times$$
$$195.7 \ cal./g.$$
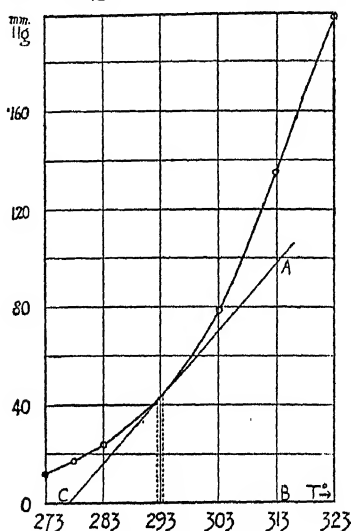
Fig. 2—Vapour Pressure of Ethyl Alcohol

5. The following figures give the b.p. of water ($t°$) and of calcium chloride solution (c = 30 g. $CaCl_2$/100 g. H_2O) ($t'°$) under a pressure of p mm.:

p	..	600	480	360	280	240	180
$t°$	..	93·5	87·6	80·3	74·35	70·6	64·15
$t'°$	..	99·25	93·2	85·75	79·55	75·75	69·10

Show graphically that Dühring's rule holds for this solution, and by plotting the vapour-pressure curve of water on the same axes read off the pressure under which the above solution will boil at 86°.

Use (47), the reference substance being water. This equation shows that the plot of T'_A, the b.p. of the solution under pressure p', against T'_B, the corresponding b.p. of water, should give a straight line for all values of p'. Plot t' (ordinate) against t (abscissa). The points lie almost exactly on a straight line, showing that Dühring's rule holds with great accuracy. On the same graph plot p (ordinate) against t for water (p. 142). To find at what pressure the solution boils at 86°, find the point on the curve corresponding to $t' = 86°$; the intersection of the ordinate of this point with the vapour-pressure curve gives the required pressure (367 mm.).

6. Find the mean heat of dissociation of NH_4HS from the following dissociation pressures and temperatures:

p (mm.)	175	212	259	322	410	501
t (°C.)	9·5	12	15	18	22	25·1

NH_4HS (solid) $\rightleftharpoons$ $NH_3 + H_2S$; $\therefore$ $n = 2$ and $\Delta V = 2RT/p$; $\therefore$ λ_d $= 2 \times 4\cdot576\, T_1\, T_2\, \log(p_2/p_1)/(T_2 - T_1)$.

T_1	T_2	$\log p_2/p_1$	λ_d
282·5	285	0·0833	$2 \times 4\cdot576 \times 282\cdot5 \times 285$ $\times\, 0\cdot0833/2\cdot5 = 24{,}540$ cal.
288	291	0·0946	$2 \times 4\cdot576 \times 288 \times 291$ $\times\, 0\cdot0946/3 = 24{,}190$ cal.
295	298·1	0·0870	$2 \times 4\cdot576 \times 295 \times 298\cdot1$ $\times\, 0\cdot0870/3\cdot1 = 22{,}520$ cal.

The mean value of λ_d is *23,750 cal./mol* (obs. 22,800).

7. Calculate the heat of hydration of Na_2HAsO_4, $7H_2O$ to Na_2HAsO_4, $12H_2O$ from the following dissocation pressures (p) and vapour pressures of water (p_0):

t (°C.)	..	..	25	30	35
p (mm.)	..	..	11·10	15·25	20·74
p_0 (mm.)	..	..	23·76	31·83	42·19

Na_2HAsO_4, $7H_2O + 5H_2O \rightleftharpoons Na_2HAsO_4$, $12H_2O$; $\therefore n = 5$. The values of $\log(p_0/p)$ for $T = 298°$, $303°$, and $308°$ are 0·3305, 0·3196, and 0·3084 respectively. From $(48a)$, $Q = 5 \times 4\cdot576 \times 298 \times 303$ $(0\cdot3196 - 0\cdot3305)/(303 - 298) = -4504$ cal. $Q = 5 \times 4\cdot576 \times$ $303 \times 308(0\cdot3084 - 0\cdot3196)/(308 - 303) = -4783$ cal. $Q = 5 \times$ $4\cdot576 \times 298 \times 308(0\cdot3084 - 0\cdot3305)/(308 - 298) = -4641$ cal. The mean value is *4640 cal.* per mol of salt (evolved).

EXERCISES.—VI

1. The vapour pressure of liquid Cl_2 is given by $\log p$ (mm.) $= -1160/T + 7\cdot773$. Calculate the mean heat of vaporization per mol.

2. The value of L_e for *n*-heptane is 78·32 cal./g. at 97·5°. The vapour pressure of the liquid is $\log p$ (mm.) $= 7\cdot36624 - 1534\cdot34/T - 49341/T^2$. If the specific volume of the liquid is 1·5 at 97·5°, calculate the specific volume of the vapour at 100° and 750 mm.

3. The b.p. (°C.) of liquid O_2 is given by $-183 + 0\cdot01258(p - 760) - 0\cdot000007(p - 760)^2$, where p is the pressure in millimetres. Calculate L_e under a pressure of 760 mm.

4. The vapour pressure of pure O_2 is as follows:

T (°K.)	..	104·2	120·0	136·0	147·8	158·4	164·7
p (mm.)	..	4·8	33·8	146·6	334·0	611·8	840·8

Assuming λ_e to be independent of T, find its value graphically. Determine also the normal b.p. of O_3.

5. The vapour pressure of liquid Se is given by $\log p$ (mm.) $= -4722/T + 10\cdot733$ and that of solid Se by $\log p$ (mm.) $= -7644/T + 16\cdot692$. Calculate the m.p. of liquid Se.

6. The saturated vapour pressure of CO_2 is $4\cdot6$ atm. at $-172\cdot2°$ and $6\cdot3$ atm. at $-168\cdot2°$. If $t_c = -139\cdot5°$ C. and $p_c = 35\cdot5$ atm., calculate λ_e at the b.p.

7. The vapour pressure of C_2H_6 between $0\cdot0245$ and $2\cdot1441$ atm. is given by $\log p$ (atm.) $= -780\cdot24 / T + 4\cdot2563 - 0\cdot000103\,T - 9\cdot3 \times 10^{-10}\,(T - 238)^4$. What is the b.p. of the liquid? What is its mol. heat of evaporation at this temperature? Compare the latter figure with that obtained without assuming the gas laws if the specific volume of saturated ethane vapour is 14,511 c.c./mol and that of the liquid 4 c.c./g.

8. If T_p is the b.p. of a liquid at p mm. (not far removed from 760 mm.) and T is the b.p. at 760 mm., then according to *Crafts' rule*:

$$T - T_p = cT(760 - p), \quad \ldots \quad (49)$$

where $c = 1/T \cdot dT_p/dp$, a constant for a given liquid. For non-associated liquids $c = 1\cdot2 \times 10^{-4}$ approx.

The b.p. of argon is $-186\cdot2°$ at $757\cdot3$ mm. If $c = 1\cdot35 \times 10^{-4}$, calculate the normal b.p.

9. If the vapour pressure of C_6H_6, p (mm.), is given by: $\log p = 7\cdot2621 - 1402\cdot46/T - 51{,}387\cdot5/T^2$, find at what pressure C_6H_6 will boil at 90° and at what temperature it will boil under a pressure of 300 mm.

10. Test graphically the validity of Dühring's vapour-pressure rule from the following data, T_a being the b.p. (°K.) of NaCl Aq. and T_b that of H_2O under p mm.:

p	..	767	335	266·3	206·9	154·2	133	103·3	50·3
T_a	..	1703	1604	1588	1571	1524	1511	1500	1429
T_b	..	373·2	351·6	346·1	340·2	333·7	330·5	325·2	311·2

11. According to Henglein T_a and T_b (see previous exercise) are related by the equation,

$$\ldots \ldots (50)$$

where l and m are constants. Calculate the b.p. of Hg under 1 atm. from the following figures:

p (mm.)	..	199	548	2934	22·3 (atm.)
T_a (Hg)	..	473	613	713	873
T_b (H_2O)	..	292	364	416	492

12. The vapour pressure of saturated NaCl solution between 24° and 50° is given by p (mm.) $= K[(T - l)/T]^{50}$ where $l = 78\cdot116$ and $\log_{10}K = 7\cdot85418$. Using this as an extrapolation formula calculate the b.p. of the solution.

13. The b.p. of C_6H_6 is 80·3° and that of C_6H_5F 85·1°. The Bertrand vapour-pressure equation holds for C_6H_6 with $\log_{10}A = 7·198932$, $B = 63·7164$, and $n = 50$ (p in mm.). At what temperature is the vapour pressure of C_6H_5F 881 mm. and at what temperature is it 36 mm.? (Use Dühring's rule.)

14. With the help of data in the previous exercise show that the vapour pressure of C_6H_5Cl (b.p. 132° C.) is 292·7 mm. at 100° C.

15. The vapour pressure of Hg over the temperature range 120° to 450° C. is given by $\log p$ (mm.) $= 9·9073436 - 3276·628/T - 0·6519904 \log T$. Find an expression for the latent heat of evaporation of Hg as a function of T.

16. The vapour pressure of Te is $1·86 \times 10^{-2}$ atm. at 671° C. and $4·40 \times 10^{-3}$ atm. at 578° C. Calculate the mean heat of evaporation.

17. The vapour pressure of I_2 between 0° and 100° is given by the formulæ: $\log p$ (mm.) $= -106·4 + 46·61 \log T - 0·03168 T = 9·7522 - 2863·5/(T - 19)$. What is the mean heat of sublimation of I_2 over this range?

18. The vapour pressure of solid cyanogen is given by $\log p$ (mm.) $= -1695·12/T + 9·6553$, and that of liquid cyanogen by $\log p$ (mm.) $= -1818·55/T - 5·0813 \log T + 22·3008$. Calculate: (a) the mol. heat of sublimation (independent of T); (b) the latent heat of evaporation, λ_e, as a linear function of T; (c) λ_e at the b.p.; (d) the temperature and pressure corresponding to the triple point; and (e) the latent heat of fusion at the triple point (when $\lambda_s = \lambda_e + \lambda_f$).

19. From the following values for the dissociation pressure of $CaCO_3$ deduce the heat of reaction at constant pressure at 700°:

T (°C.)	600	650	700	750	800
Pressure (mm. Hg)	2·35	8·2	25·3	68·0	168·0

(Lond. B.Sc. Hons., 1925.)

20. Calculate the heat of hydration of $CuSO_4, 3H_2O$, to $CuSO_4, 5H_2O$, the dissociation pressure being 7·92 mm. at 25°; 11·74 mm. at 30°; and 17·01 mm. at 35°. (Use data in Example 7, p. 23.)

(iii) Heats of Reaction.

(1) **Enthalpy.**—The *heat of a reaction* (absorbed) occurring at constant vol. ($dv = 0$) is the increase in *intrinsic energy*, U, of the system:

$$Q_v = U_2 - U_1 = \Delta U. \quad . \quad . \quad . \quad (51)$$

The heat of a reaction occurring at constant pressure is the increase in *enthalpy* (or *heat content*) of the system, $H = U + pv$. f

$$\begin{aligned}
Q_p &= Q_v + A = U_2 - U \\
&= (U_2 + pv_2) - (U_1 + pv_1) = H_2 - H_1 = \Delta H. \quad (52)
\end{aligned}$$

(D 892)   3

In thermochemistry, it is usual to regard *heat evolved* as *positive*; we may write it Q, so that *

$$Q = -\mathrm{Q}.$$

$$\therefore\ Q_v = \mathrm{U}_1 - \mathrm{U}_2 = -\Delta\mathrm{U},\ \text{and}$$

$$Q_p = \mathrm{H}_1 - \mathrm{H}_2 = -\Delta\mathrm{H}. \qquad . \quad (51a, 52a)$$

In reactions involving only solids and liquids the vol. changes are negligible and $\Delta\mathrm{H} = \Delta\mathrm{U}$, approx. In the case of gases (assumed ideal),

$$Q_p - Q_v = \Delta\mathrm{U} - \Delta\mathrm{H} = -\mathrm{A}$$
$$= p(v_1 - v_2) = (n_1 - n_2)\mathrm{RT}. \quad . \quad (53)$$

At 18°, with Q in g. cal.

$$Q_p - Q_v = 580\,(n_1 - n_2). \quad . \quad . \quad . \quad (53a)$$

(2) **Hess's Law of Constant Heat Summation.**—The heat of a chemical reaction depends only on the initial and final states (p, or v, constant).

(3) **Heat of Formation** of a compound is the heat evolved, Q_v or Q_p, in the formation of 1 mol from the elements. It is the defect in energy or enthalpy of 1 mol of the substance as compared with that of the component elements at the same temperature, which are arbitrarily assumed to have zero energy or enthalpy. (This assumption can be made only where energy *differences* are concerned, not, e.g., in calculations of entropy.)

The equations:

$$\mathrm{H}_2\,(g) + \tfrac{1}{2}\mathrm{O}_2\,(g) = \mathrm{H}_2\mathrm{O}\,(l) + 68{,}400\ \text{cal}.$$
$$\mathrm{H}_2\,(g) + \tfrac{1}{2}\mathrm{O}_2\,(g) = \mathrm{H}_2\mathrm{O}\,(l);\ \Delta\mathrm{H} = -68{,}400\ \text{cal}.,$$
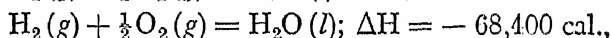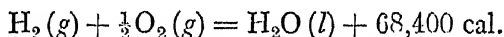
both signify that in the combination of 2 g. of H_2 gas with 16 g. of O_2 gas, both at room temperature, to form 18 g. of liquid water, also at room temperature, the pressure being constant at 1 atm., then 68,400 cal. are *evolved* ($Q_p = -\Delta\mathrm{H}$). The second equation is in the form commonly used in America; the enthalpy (heat content) of the substance on the right is less than that of the substances on the left by 68,400 cal.

(4) **Heat of Reaction** is equal to the sum of the heats of

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* In writing out exercises, Q may be written as $\mathcal{Q}$.

formation of the products less the sum of the heats of formation of the reactants.. This follows from Hess's law.

When the heat of a reaction is to be found from those of a number of others, write the equations of the reactions, each with its heat of reaction on the right, one below the other, so that on addition all symbols cancel except those composing the reaction in question.
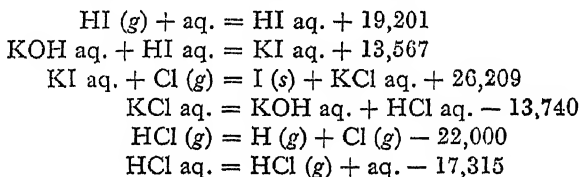
EXAMPLES.—1. Calculate the heat of the reaction $H_2(g) + I_2(s) = 2HI(g)$ from the following heats of reaction: (i) $HI(g) + aq. = HI\ aq. + 19,201$ cal.; (ii) $KOH\ aq. + HI\ aq. = KI\ aq. + 13,567$ cal.; (iii) $KI\ aq. + Cl(g) = I(s) + KCl\ aq. + 26,209$ cal.; (iv) $KOH\ aq. + HCl\ aq. = KCl\ aq. + 13,740$ cal.; (v) $H(g) + Cl(g) = HCl(g) + 22,000$ cal.; (vi) $HCl(g) + aq. = HCl\ (aq.) + 17,315$ cal.

In accordance with the above rule the following equations are added:

$$HI(g) + aq. = HI\ aq. + 19,201$$
$$KOH\ aq. + HI\ aq. = KI\ aq. + 13,567$$
$$KI\ aq. + Cl(g) = I(s) + KCl\ aq. + 26,209$$
$$KCl\ aq. = KOH\ aq. + HCl\ aq. - 13,740$$
$$HCl(g) = H(g) + Cl(g) - 22,000$$
$$HCl\ aq. = HCl(g) + aq. - 17,315$$

whence $H_2(g) + I_2(s) = 2HI(g) - 11,844\ cal.$

NOTE.—aq. denotes a large (unknown) amount of water.

2. The heat of neutralization of HNO_3 by $NaOH$ is 13,680 cal. and of dichloracetic acid 14,830 cal. One equivalent of $NaOH$ aq. is added to a mixture of 1 equivalent of HNO_3 and $CHCl_2 . COOH$; the heat evolved is 13,960 cal. Calculate the relative strengths of the two acids.

Let x represent the fraction of base neutralized by the HNO_3. Then $xHNO_3 + xNaOH = xNaNO_3 + xH_2O + 13,680x$; and $(1 - x)\ CHCl_2 . COOH + (1 - x)\ NaOH = (1 - x)\ CHCl_2COONa + (1 - x)\ H_2O + 14,830\ (1 - x)$. Hence $13,680x + 14,830\ (1 - x) = 13,960$, or $x = 0.77$ and $1 - x = 0.23$. The relative strengths, therefore, are $HNO_3 : CHCl_2 . COOH = 0.77 : 0.23 = 10 : 3.$

3. Calculate the enthalpy increase when 1 mol. of H_2 ($c_p = 3.5$) is heated from $0°$ to $50°$ at 1 atm. Find, also, the value of ΔU. (Assume ideal gas.)

$\Delta H = Q_p = 50 \times 3.5 \times 2 = 350\ g.\ cal.$; and since $C_p - C_v = R = 1.99$ cal./mol, $C_v = C_p - R = 2 \times 3.5 - 1.99 = 5.01$ cal./mol and $\Delta U = Q_v = 50 \times 5.01 = 250\ g.\ cal.$

EXERCISES.—VII

1. From the appended equations calculate the heat of formation of NH_3 from gaseous H_2 and N_2, (a) in the dry state, (b) in solution in water: $4NH_3 + 3O_2 = 2N_2 + 6H_2O + 362,400$; $2H_2 + O_2 =$

$2H_2O + 136,800$; $NH_3 + aq. = NH_3$ aq. $+ 8400$ cal. (Camb. Nat. Sci. Tripos, 1915.)

2. The heat of formation of dilute NaOH solution from Na, O, H, and aq. is 111,810 cal.; that for HCl solution is 39,315 cal. The heat of neutralization of dilute NaOH by dilute HCl is 13,745 cal., and the heat of solution of NaCl in diluted solution is -1180 cal. Calculate the heat of formation of NaCl from its elements if the heat of formation of liquid water is 68,360 cal./mol.

3. The heat liberated by the solution of 1 g. atom of K in a large amount of water is 48,100 cal. The heat of dilute solution of KOH is 13,290 cal., and the heat of formation of liquid water from its elements is 68,360 cal./mol. Calculate the heat of formation of KOH from its elements.

4. The heat of reaction of SO_2Cl_2 with a large quantity of water is 62,900 cal. Given the following heats of reaction calculate the heat of formation of SO_2Cl_2 from SO_2 and Cl_2: $SO_2 + \frac{1}{2}O_2 + aq. = SO_3$ aq. $+ 71,330$; $H_2 + Cl_2 + aq. = 2HCl$ aq. $+ 78,600$; $H_2 + \frac{1}{2}O_2 = H_2O$ (liq.) $+ 68,360$.

5. The heat of solution of Al in dilute HCl to form $AlCl_3$ is 119,880 g. cal./mol of Al, and the heat of formation of dilute HCl from H_2, Cl_2, and water is 39,315 cal./mol. If the heat of solution of $AlCl_3$ is 76,845 cal./mol, calculate the heat of formation of anhydrous $AlCl_3$.

If the heat of neutralization of $Al(OH)_3$ is 55,920 cal., what is its heat of formation? The heat of formation of water is 68,360 cal./mol.

6. If the heat of neutralization of CuO by HCl is 15,270 cal. per mol of oxide, and the heat of dilute solution of anhydrous $CuCl_2$ is 11,080 cal., calculate the heat of formation of anhydrous $CuCl_2$ from its elements, given that that of CuO is 37,160 cal.

7. The heat of solution of Cu_2O in dilute HCl is 11,630 cal. per mol of oxide. Using data in Example 6, calculate the heat of formation of Cu_2O.

8. Find the heat of formation of H_2SO_4 from the following: heat of solution of SO_2 (g), 8000 cal.; heat of dilute solution of H_2SO_4, 18,000 cal.; heat of formation of HCl (g), 22,000 cal./mol; heat of dilute solution of HCl (g), 17,300 cal.; heat of formation of SO_2 from solid S, 70,200 cal./mol; heat of formation of liquid water from its gaseous elements, 68,400 cal./mol; heat of oxidation of SO_2 in aq. solution by Cl_2 (g), 73,900 cal.

9. If the heat of combustion of sucrose ($C_{12}H_{22}O_{11}$) is 1,349,000 cal./mol show that its heat of formation is *about* 525,300 cal./mol, given that the heats of formation of CO_2 and H_2O (l) are 94,800 and 68,360 cal. respectively.

10. Using some of the data in Example 9, calculate the heat of formation of C_2H_6 at constant vol. if the heat of combustion of this gas is 369,000 cal./mol at 25°.

11. The heat of neutralization of a strong base with a strong acid is 13,700 cal. at 20°. The heat of neutralization of HF is accompanied by the evolution of 16,270 cal. What is the heat of dissociation of HF?

12. The reduction of AuBr by SO_2 produces the β modification of Au: $2AuBr + H_2O + SO_2$ aq. $= 2HBr$ aq. $+ SO_3$ aq. $+ 2Auβ + 42,760$ cal.; similarly in the case of the reaction $3AuBr + HBr$ aq. $= HAuBr_4$ aq. $+ 2Auβ + 3652$ cal. Calculate the heat of the reaction $Auβ = Au$ from the following data: $H_2 + Br_2 + $ aq. $= 2HBr$ aq. $+ 2 \times 28,380$ cal.; $H_2 + \frac{1}{2}O_2 = H_2O + 68,360$ cal.; SO_2 aq. $+ \frac{1}{2}O_2 = SO_3$ aq. $+ 63,630$ cal.; $Au + 3Br + HBr$ aq. $= HAuBr_4$ aq. $+ 12,785$ cal.
Calculate also the heat of formation of AuBr from its elements.

13. The heat of dissociation of H_2S is 19,700 cal./mol, whereas its heat of formation from H_2 gas and solid S is 2700 cal./mol (evolved). If the heat of vaporization of solid S is 12,200 cal./g. atom at 300°, calculate the approx. heat of the dissociation $S_8 \rightleftharpoons 4S_2$.

(5) Kirchhoff's Equation.—According to this (*C. T.*, § 22):

$$dQ/d\mathrm{T} = -dQ/d\mathrm{T} = \Sigma\, n_i C_i - \Sigma\, n_f C_f. \qquad (54)$$

$$\therefore\ Q = Q_0 + \int_0^{\mathrm{T}} (\Sigma\, n_i C_i - \Sigma\, n_f C_f)\, d\mathrm{T}, \qquad (54a)$$

where $\Sigma\, n_i C_i$ represents the sum of the molecular heat capacities of the initial substances ($n = $ number of mols), $\Sigma\, n_f C$ that of the products of reaction, all at constant vol. *or* constant pressure, according as Q is Q_v or Q_p.

EXAMPLE.—The molecular heats of NH_3 (at constant pressure) H_2, and N_2 (at constant vol.) are: NH_3, $C_p = 8.04 + 0.0007\,T + 0.0_551T^2$; H_2, $C_v = 4.66 + 0.0007\,T$; N_2, $C_v = 4.92 + 0.00017\,T + 0.0_531T^2$. Calculate the heat of formation of NH_3, at constant pressure from its elements at 700° C., given that its value at 20° C. is 11,890 cal./mol.
To obtain the answer for conditions of constant pressure convert all specific heats to constant pressure: $C_p = C_v + R = C_v + 2$ (cal./mol)/1°. The reaction is: $N_2 + 3H_2 = 2NH_3$; since we are finding Q_p for 1 mol of NH_3 we rewrite it: $\frac{1}{2}N_2 + \frac{3}{2}H_2 = NH_3$.

$$N_2 : \tfrac{1}{2}C_p = \tfrac{1}{2}(C_v + R) = \quad 3.46 + 0.0_485\,T + 0.0_6155\,T^2$$
$$H_2 : \tfrac{3}{2}C_p = \tfrac{3}{2}(C_v + R) = \quad 9.99 + 0.0_21050\,T$$
$$\therefore \Sigma\, n_i C_i = 13.45 + 0.001135\,T + 0.0_6155\,T^2$$
$$NH_3 : 1C_p = \Sigma\, n_f C_f = \quad 8.04 + 0.0007\,T + 0.0_551\,T^2$$
$$\therefore\ dQ_p/d\mathrm{T} = \Sigma\, n_i C_i - \Sigma\, n_f C_f = \quad 5.41 + 0.000435\,T - 0.0_54945\,T^2$$

$$\therefore\ Q_p = Q_0 + 5.41T + 0.0_22175\,T^2 - 0.0_51648\,T^3.$$

When T $= 293°$ K., $Q_p = 11,890$ cal.; substitute and find Q_0.

$$11,890 = Q_0 + 1585 + 18.68 - 41.47; \quad \therefore\ Q_0 = 10,328 \text{ cal.}$$

Hence, the relation between Q_p and T is given by: $Q_p = 10,328 + 5.41\,T + 0.0_22175\,T^2 - 0.0_51648\,T^3$, and by putting T $= 973°$ K. we

find that the heat of formation of 1 mol of NH_3 from its elements at 700° C. is *14,298 cal.*

EXERCISES.—VIII

1. The heat of the reaction $H_2 + I_2$ (*g*) $= 2HI$ (*g*) at constant pressure is 16,000 cal. at 25° C. Calculate the heat of formation per mol of HI from its gaseous elements at 0° C., given the following mol. heats: HI, $C_p = 6·5 + 0·0016\,T$; I_2 (vap.), $C_p = 6·5 + 0·0038\,T$; H_2, $C_p = 6·5 + 0·0017\,T$.

2. The mol. heats at constant vol. of Cl_2, HCl, and H_2 are $5·704 + 0·0005\,T$; $4·90 + 0·0009\,T$; $4·50 + 0·0017\,T$. Find an expression for the heat of formation of HCl at constant pressure and find its value at 1000° C., given that the heat of formation of 1 mol of HCl from its elements at 25° and 1 atm. pressure is 22,000 cal.

3. The specific heats at constant volume of N_2, O_2, and NO are as follows: C_v $(N_2) = 5·014 - 0·0_3504\,T + 0·0_68376\,T^2 - 0·0_91449\,T^3$; $C_v(O_2) = 5·156 - 0·0_3587\,T + 0·0_68567\,T^2 - 0·0_91481\,T^3$; and C_v (NO) $= 5·102 - 0·000564\,T + 0·0_69554\,T^2 - 0·0_91934\,T^3$. The heat of the reaction $N_2 + O_2 = 2NO$ is 46,000 cal. (absorbed) at 2114° K. What is the heat of the reaction at 1000° K.? (R $= 1·985$ cal./mol.)

4. The heat of combustion at constant pressure of CO is 68,300 cal./mol and that of graphite 94,000 cal., the temperature being 300° K. From the following true specific heats at constant vol. calculate the heat of the reaction $C + CO_2 \rightleftharpoons 2CO$ at 1000° K. at constant vol. C_v (graphite) $= -1·51 + 1·56 \times 10^{-2}T - 1·35 \times 10^{-5}T^2 + 0·455 \times 10^{-8}T^3$; $C_v(CO_2) = 3·77 + 1·24 \times 10^{-2}T - 0·57 \times 10^{-5}T^2 + 0·0002 \times 10^{-8}T^3$; $C_v(CO) = 4·84 + 0·054 \times 10^{-2}T$.

5. The heat of the reaction $CO + \frac{1}{2}O_2 = CO_2$ at constant pressure is 68,000 cal. at 0°. The true mol. heats of the gases at constant vol. are: CO_2, $5·106 + 0·003344\,T$; CO and O_2, $4·68 + 0·000268\,T$. Find the heat of formation of CO_2 at constant pressure at 2500° C.

6. The molecular heat of H_2 at constant vol. is $4·5 + 0·0009\,T$, whilst that of O_2 is $4·5 + 0·0005\,T$, and that of steam $6·81 - 0·0019\,T + 0·00000222\,T^2$. The heat of combustion of 1 g. of H_2 at constant pressure to form liquid water at 0° is 34,000 cal., and the mol. heat of evaporation of water at 0° is 600 cal. Calculate the heat of formation, at constant pressure, of 1 mol of steam from its elements at 100°.

7. You are given $H_2 + \frac{1}{2}O_2 = H_2O$ (vap.) $+ 57,800$ cal. at 15° C. and $CO + \frac{1}{2}O_2 = CO_2 + 68,000$ cal. at 15° C. Find the heat change involved in the water-gas reaction: $H_2 + CO_2 = H_2O + CO$ at room temperature, and, starting from the First Law of Thermodynamics, show how the heat change at *any* temperature can be calculated from the following data: H_2, $C_p = 6·50 + 0·0009\,T$; CO_2, $C_p = 7·0 + 0·0071\,T - 0·0000019\,T^2$; CO, $C_p = 6·50 + 0·0010\,T$; H_2O (vap.), $C_p = 8·81 - 0·0019\,T + 0·00000222\,T^2$. Calculate its value at 2000° K. (Manc. Hons. Chem., 1925.)

(iv) Entropy and Free Energy.

(1) **Entropy.**—The increase in *entropy* of a system, $d\mathrm{S}$,

due to the *reversible* absorption of a quantity of heat δQ at temperature T, is defined as $\delta Q/T$; or

$$\int_{A}^{B} \delta Q/T = S_B - S_A, \quad \ldots \quad (55)$$

where A and B represent two states of the system and S_A, S its entropies in these states. Equation (55) holds for *reversible* changes only, although the values of S_A or S_B depend only on the state of the system, the entropy of which is independent of the way in which it is brought into that state, whether reversibly or otherwise.

If unit mass of a substance is heated reversibly under specified conditions the entropy increase is: $\Delta s = s_2 - s_1 = \int \delta Q/T = \int c \, dT/T$, whence

$$ds/dT = c/T. \quad \ldots \ldots \quad (56)$$

The particular value of c appropriate to the conditions (c_v or c_p) must, of course, be used. Similarly, the entropy increase attending the transition of unit mass of a substance from one state to another at the transition temperature T is (T = constant)

$$\Delta s = \int \delta Q/T = (1/T) \int \delta Q = L/T, \quad . \quad (57)$$

where L is the latent heat of transition per g. According to *Trouton's rule* the entropy increase per mol on evaporation is constant for all *normal* (i.e. unassociated, or *non-polar*) liquids:

$$\lambda_e/T_s = 21 \text{ cal.}/1^\circ, \quad \ldots \ldots \quad (58)$$

where T_s is the absolute b.p. The rule is very approximate; substances for which λ_e/T_s exceeds 21 cal./1° are considered to be associated.

The entropy change attending the conversion of 1 mol of ideal gas from p_1, T_1, v_1 to p_2, T_2, v_2 is (C_v and C_p constant):

$$\Delta S = C_v \ln T_2/T_1 + R \ln v_2/v_1 = C_p \ln T_2/T_1 - R \ln p_2/p_1$$
$$= C_v \ln p_2/p_1 + C_p \ln v_2/v_1. \quad \ldots \ldots \ldots \quad (59)$$

For a gas obeying van der Waals' equation (79):

$$\Delta S = C_v \ln T_2/T_1 + R \ln(v_2 - b)/(v_1 - b). \quad (59a)$$

Units.—From (55) it is seen that entropy is expressed in

cal./1° when δQ is in cal. Numerical values of S for *solid* substances may be referred to the value $S = 0$ for the solid at 0° K., in accordance with Nernst's heat theorem. Values of ΔS for solid elements and compounds are given in entropy tables (p. 38). For *gases* or *solutions* no such zero of entropy may be assumed. On the basis of the quantum theory and Nernst's heat theorem the *absolute* entropy of a monatomic gas (mol. wt. M) at T° and p atm. is (in cal./1°/mol.):

$$S = 11 \cdot 44 \, \log T - 4 \cdot 576 \, \log p + 6 \cdot 864 \, \log M - 2 \cdot 3. \quad (60)$$

At $T = 0$ this ceases to have a finite value.

EXAMPLES.—1. The vapour pressure of Br_2 at 25° is 213 mm. and $\lambda_e = 7570$ cal. at the same temperature. If the entropy of liquid Br_2 is 33 units at 25°, calculate that of Br_2 vapour at 1 atm.

The total change must be divided into reversible changes: Br_2 (*l*; 213 mm.) — Br_2 (*g*; 213 mm.); Br_2 (*g*; 213 mm.) — Br_2 (*g*; 760 mm.). The entropy change attending the isothermal evaporation at 213 mm. is $7570/298 = 25 \cdot 4$ cal./mol. For the second change $\Delta S = R \ln v_2/v_1 = R \ln p_1/p_2 = 2 \times 2 \cdot 3 \times \log 213/760 = -2 \cdot 5$ cal./mol. Hence the total entropy change is $25 \cdot 4 - 2 \cdot 5 = 22 \cdot 9$ cal./mol, and the entropy of Br_2 vapour is $33 + 22 \cdot 9 = 55 \cdot 9$ *units* at 1 atm. and 25°, referred to that of the liquid at 25° C. as zero.

2. Calculate the entropy of liquid Br_2 per g. atom at 25° from the following values of c_p (cal./g. atom):

T (°K.) ..	14·9	17·3	20·2	26·6	33·1	48·6	55·3
c_p	0·914	1·18	1·52	2·25	2·90	3·98	4·33

T (°K.) ..	71·8	90·5	152·7	183·0	209·3	252·?
	4·73	5·05	5·9	6·27	6·56	7·18

Assume that at sufficiently low temperatures $c_p = aT^b$, where a and b are constants characteristic of the substance. The m.p. of $Br_2 = 265 \cdot 9°$ K. and the latent heat of fusion = 1290 cal./g. atom at the m.p.; the specific heat of liquid bromine between the m.p. and 298° K. is constant at 8·4 cal./g. atom.

According to (56) $ds/dT = c/T$, whence $\Delta s = \int_{T_1}^{T_2} c \, dT/T = \int_{T_1}^{T_2} c \, d(\ln T)$. In other words (cf. p. 2) the entropy difference of a substance between the states T_2 and T_1 is equal to the area enclosed by the graph of c against $\ln T$, the $\ln T$ axis, and the ordinates at T_2 and T_1. Hence, first plot c against $\ln T$ (= $2 \cdot 3 \log T$). The extrapolation to $T = 0$ is somewhat uncertain (see fig. 3), so the area between $T = 15 \cdot 85°$ K. ($\log T = 1 \cdot 20$) and the m.p., $T = 265 \cdot 9°$ K. ($\log T = 2 \cdot 43$), is determined. This area is $26 \cdot 2$ squares. But the $\log T$ scale is

one-fifth of the c_p scale. Hence the required area = area had the two scales been identical = $\frac{1}{5} \times 26\cdot2 = 5\cdot24$ squares. Convert the log T scale to lnT $\therefore$ true area = $2\cdot3 \times 5\cdot24 = 12\cdot05$ units = entropy difference between $15\cdot85°$ K. and $265\cdot9°$ K.

Below $15\cdot85°$ K. it may be assumed that $c_p = aT^b$. To find the values of a and b plot $\log c$ against $\log T$ (inset, fig. 3): $\log c = \log a + b \log T$. The slope of the straight line is $1\cdot3$ and hence $a = 0\cdot0306$.
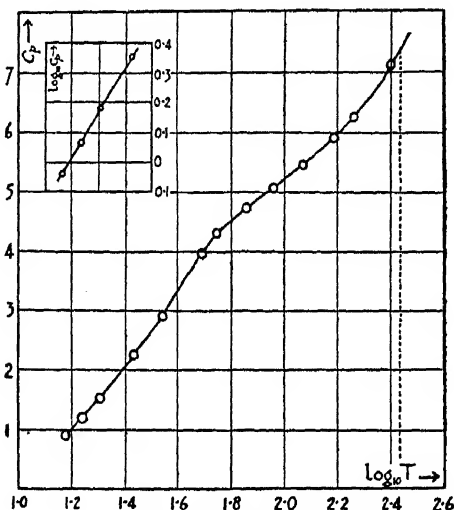
Fig. 3.—Entropy of Bromine

The entropy difference between $0°$ and $15\cdot85° = \int_0^{15\cdot85} c\,dT/$ $0\cdot0306/1\cdot3 . [T^{1\cdot3}]_0^{15\cdot85} = 0\cdot85$ units. This value is probably too high because at exceedingly low temperatures b is nearer 3. The entropy of Br_2 at the m.p. is thus $12\cdot05 + 0\cdot85 = 12\cdot9$ units.

The entropy change attending fusion is $1290/265\cdot9 = 4\cdot85$ units, and that attending the heating of liquid bromine from $265\cdot9°$ to $298°$ $= \int c\,dT/T = 8\cdot4\,[lnT]_{265\cdot9}^{298} = 8\cdot4 \times 2\cdot3[2\cdot4742 - 2\cdot4247] = 0\cdot95$ units.

Hence entropy of liquid Br_2 at $298°$ K. = difference between the entropies at $25°$ C. and $-273°$ C. = $12\cdot9 + 4\cdot85 + 0\cdot95 = 18\cdot7$ units/g. atom.

3. What is the entropy increase attending the expansion of 10 mol. of O_2 at $25°$ from 20 l. to 200 l.?

$$\Delta S \qquad = 10R \ln(v_2 \qquad : 45\cdot76 \log10 = 45\cdot76 \text{ units.}$$

EXERCISES.—IX

1. Find ΔS attending the conversion of unit mass of H_2O (liq.) at $0°$ into steam at $150°$ and 1 atm., given that $L_e = 536$ cal./g. for water and $\bar{c}_p = 0·477$ for steam.

2. Find ΔS for 1 g. of H_2O under 1 atm. pressure at $0°$ and at $100°$; $\bar{c} = 1$.

3. Calculate ΔS for 1 g. of liquid $SnCl_4$ between $-33°$ (m.p.) and the liquid at $114°$ (b.p.), the pressure being 1 atm. and the specific heat of the liquid $0·148$ cal./g.

4. Calculate ΔS for the conversion of 2 mols of H_2 from 30 l. at 2 atm. to 100 l. at 1 atm. $(C_p = 7·4)$.

5. For NH_3 $C_v = 6·70$ cal./mol, whilst the van der Waals' constant b is $37·09$ c.c./mol. Calculate ΔS for the expansion of 1 mol of NH_3 from $22·6$ l. at $10°$ C. to 25 l. at $20°$ C.

6. Calculate the entropy of He at $0°$ and 1 atm.

7. Calculate ΔS attending the heating of 1 mol of PbI_2 from $20°$ K. to $100°$ K., given the following specific heats (cal./mol.):

T (°K.) ..	22·3	26·2	38·2	50·6	62·1	89·4	95·6
C_p	7·1	7·9	10·7	13·2	14·8	17·1	17·3

8. The entropy increase attending the isothermal diffusion of n_1 mols of an ideal gas occupying v_1 into n_2 mols of another ideal gas occupying v_2 is

$$\Delta S = R[n_1 \ln(v_1 + v_2)/v_1 + n_2 \ln(v_1 + v_2)/v_2]. \quad . \quad (61)$$

Calculate ΔS for the diffusion of 1 mol of H_2 occupying $22·4$ l. at $0°$ and 760 mm. into 2 mols of N_2 occupying $44·7$ l.

(2) **Free Energy.**—The maximum work, A, obtainable from a system undergoing *a reversible change* at *constant temperature* is measured by the diminution of a magnitude characterized by the state of the system, called *free energy*, $F = U - TS$:

$$A = Q - \Delta U = T \Delta S - \Delta U$$
$$= (U_1 - TS_1) - (U_2 - TS_2) = F_1 - F_2 = -\Delta F. \quad (62)$$

The absolute value of F for a substance is unknown, since it involves an arbitrary linear function of T; only its changes can be measured, and Hess's law applies to these.

(3) **Thermodynamic Potential.**—Systems undergoing isothermal reversible changes at *constant pressure* yield an amount of work which, when diminished by the external work due to change of vol., measures the diminution of a function

Z, the *thermodynamic potential*, which depends only on the actual state of the system. Let

$$Z = F + pV = U - TS + pV. \quad . \quad . \quad (63)$$

If $p = constant$, $\Delta Z = \Delta F + p \Delta V$. But $-\Delta F =$ work performed $= A$ (at constant pressure). Hence

$$A' = A - p \Delta V = -\Delta Z = Z_1 - Z_2. \quad . \quad (63a)$$

The absolute value of Z for a substance is unknown, since it involves an arbitrary linear function of temperature; only changes in Z can be measured. As in the case of free energy, Hess's law (p. 26) is applicable to thermodynamic potential. Negative values of ΔZ for a reaction indicate that that reaction can proceed spontaneously.[*]

Illustration.—Consider a fluid under two different pressures, p_1 and p_2, the corresponding vols. being v_1 and v_2. The maximum work obtainable by passing from the initial to the final state is $\int_{v_1}^{v_2} p \, dv$ and hence $\Delta F = F_2 - F_1 = - \int_{v_1}^{v_2} p \, dv$

$= p_1 v_1 - p_2 v_2 + \int_{p_1}^{p_2} v \, dp$. But, from equation (63), $\Delta Z = Z_2$

$- Z_1 = F_2 - F_1 + p_2 v_2 - p_1 v_1$. Hence $\Delta Z = \int_{p_1}^{p_2} v \, dp$. If

the fluid is an ideal gas, $p_1 v_1 = p_2 v_2$ and $\Delta F = \Delta Z$.

(4) **Maximum Work Equation.**—For an isothermal reversible change the maximum work A $(= -\Delta F)$ is given by the equation:

$$A_T + Q_v = T(dA/dT)_{\Delta v}, \quad . \quad . \quad (64)$$

in which the interpretation of dA/dT requires careful consideration (cf. *C. T.*, p. 128).

Similarly, when the reaction occurs at constant pressure, we obtain from (63) $(A_T' = -\Delta Z)$:

$$A_T' + Q_p = T(dA/dT)_p. \quad . \quad . \quad (65)$$

Equations (64) and (65) are readily integrated with the aid of Kirchhoff's equation, (54) (see Ex. 2 below). If the specific heats of each of the initial substances and products are of the

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[*] G. N. Lewis, and American chemists in general, refer to the Z function as " free energy " and denote it by *F*. In the present book, however, the more usual nomenclature has been retained in order to avoid confusion.

form $c = a + b\mathrm{T} + d\mathrm{T}^2 + \ldots$, then application of (54) gives

$$Q = Q_0 + (\Sigma a)\mathrm{T} + \tfrac{1}{2}(\Sigma b)\mathrm{T}^2 + \tfrac{1}{3}(\Sigma d)\mathrm{T}^3 + \ldots, \quad (65a)$$

and integration of (64) and (65) gives

$$-\mathrm{A} = Q_0 - (\Sigma a)\mathrm{T}\,\ln\mathrm{T} - \tfrac{1}{2}(\Sigma b)\mathrm{T}^2$$
$$- \tfrac{1}{6}(\Sigma d)\mathrm{T}^3 - \ldots - I\,\mathrm{T}, \quad . \quad (66)$$

where I is an integration constant which can be calculated if A is known at any one temperature (e.g. at an equilibrium, or transition, temperature, where $\mathrm{A} = 0$; or by calculation from tables, as in Ex. 3).

If Q is known for a series of temperatures, but cannot readily be expressed as a function of T, then equation (65) may be integrated graphically:

$$\mathrm{A}_2/\mathrm{T}_2 - \mathrm{A}_1/\mathrm{T}_1 = \int_{\mathrm{T}_1}^{\mathrm{T}_2} Q/\mathrm{T}^2 \, . \, d\mathrm{T}.$$

A must still be known at one temperature.

In the case of reactions involving only solids the specific heats may be expressed by (33), (34), or (35). If n is the number of mols of a substance taking part in the reaction, reckoned positive if the substance is formed and negative if it disappears, then $dQ/d\mathrm{T} = -\Sigma n\,C_p = -\Sigma n\,C_v - \Sigma nk'\mathrm{T}^{3/2}$ (cf. equation 29). Then Einstein's equation for C_v gives:

$$Q = Q_0 - 3R\mathrm{T}\,\Sigma n(x/e^x - 1) - 0{\cdot}4\,\Sigma n\,k'\,\mathrm{T}^{2\cdot5}, \quad (67)$$
$$\mathrm{A} = Q_0 - 3R\mathrm{T}\,\Sigma n\,\ln(1 - e^{-x}) + 4/15\,.\,\Sigma n\,k'\,\mathrm{T}^{2\cdot5}, \quad (67a)$$

where $x = \beta\nu/\mathrm{T}$. The Nernst-Lindemann equation gives:

$$Q = Q_0 - 1{\cdot}5\,R\mathrm{T}\,\Sigma n[x/(e^x - 1) + 0{\cdot}5x/(e^{x/}\ -1)]$$
$$- 0{\cdot}4\,\Sigma nk'\mathrm{T}^{2\cdot5}, \quad . \quad . \quad . \quad . \quad . \quad (68)$$

$$\mathrm{A} = Q_0 - 1{\cdot}5\,R\mathrm{T}\Sigma n[\ln(1 - e^{-x}) + \ln(1 - e^{-x/2})]$$
$$+ 4/15\,.\,\Sigma nk'\mathrm{T}^{2\cdot5}; \quad . \quad . \quad . \quad . \quad (68a)$$

and the Debye equation (35) gives:

$$Q = Q_0 - 0{\cdot}75\,R\mathrm{T}\Sigma n[C_v/3R + 3x/(e^x - 1)]$$
$$- 0{\cdot}4\Sigma nk'\mathrm{T}^{2\cdot5}, \quad . \quad . \quad . \quad . \quad (69)$$

$$\mathrm{A} = Q_0 + 0{\cdot}25\,R\mathrm{T}\Sigma n[C_v/3R + 3x/(e^x - 1) - 12\,\ln(1 - e^{-x})]$$
$$+ 4/15\,.\,\Sigma nk'\mathrm{T}^{2\cdot5}. \quad . \quad . \quad . \quad . \quad . \quad (69a)$$

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These equations, dependent on Nernst's heat theorem, are most conveniently applied with the aid of tables. Equations (69) and (69a) may be written $Q = Q_0 - \Sigma n X - 0.4\Sigma n k' \mathrm{T}^{2.5}$ and $\mathrm{A} = Q_0 + \Sigma n Y + 4/15 \cdot \Sigma n k' \mathrm{T}^{2.5} = Q_\mathrm{T} + \Sigma n (X + Y) + 2/3 \cdot \Sigma n k' \mathrm{T}^{2.5}$, respectively. The functions X and Y, together with similar functions for equations (67) to (68a), will be found tabulated in MacDougall, *Thermodynamics and Chemistry* (1926), pp. 403 ff. Another method of applying these equations is given on p. 128.

EXAMPLES.—1. For Br_2 gas, $C_p = 7.4 + 0.001\,\mathrm{T}$, and for the liquid $C_p = 17.0 + 0.001\,\mathrm{T}$ (approx.). For Br_2, $\lambda_e = 7520$ cal./mol at $32°$ and the vapour pressure at $25°$ is 213 mm. Calculate ΔZ for the change Br_2 (*l*) $\longrightarrow Br_2$ (*g*) at $10°$, assuming the vapour to be a perfect gas.

For the change Br_2 (*l*) $\longrightarrow Br_2$ (*g*), $dQ/d\mathrm{T} = \mathrm{C}$ (*l*) $- \mathrm{C}$ (*g*) $= (17.0 + 0.001\,\mathrm{T}) - (7.4 + 0.001\,\mathrm{T}) = 9.6$; hence $Q = Q_0 + 9.6\,\mathrm{T}$. Putting $Q = -7520$ cal. and $\mathrm{T} = 305°$, we have $Q_0 = -10,448$ cal. Hence $Q = 10,448 - 9.6\,\mathrm{T}$. From (65) $\mathrm{A} = \mathrm{T} \int Q/\mathrm{T}^2 \cdot d\mathrm{T} = \mathrm{T}[-10,448/\mathrm{T} + 9.6\,\mathrm{T} \ln\mathrm{T} + \mathrm{T} \times constant]$, or $\Delta Z = -\mathrm{A}' = 10,448 + 9.6\,\mathrm{T} \ln\mathrm{T} + \mathrm{T} \times constant$. The maximum work available in the vaporization of 1 mol. of Br_2 at $25°$ is $\mathrm{A}' = \mathrm{RT} \ln v_2/v_1 = \mathrm{RT} \ln p_1/p_2 = 4.6 \times 298[2.3284 - 2.8808] = -757$ cal., or $\Delta Z = 757$ cal. at $25°$. Hence *constant* in the equation for ΔZ is -87.3 and $\Delta Z = 10,448 + 9.6\,\mathrm{T} \ln\mathrm{T} - 87.3\,\mathrm{T}$. Putting $\mathrm{T} = 283°$ we have $\Delta Z = 1080$ *cal.*

2. Find an expression for the maximum work of the reaction $CO + 2H_2 = CH_3OH$ from the following data. At $25°$ the heat of formation of CH_3OH (*l*) is 59,900 cal. and that of CO 26,150 cal., the ΔZ of formation being, respectively, $-44,500$ and $-32,500$ cal. Specific heats: H_2, $C_p = 6.65 + 0.00070\,\mathrm{T}$; CO, $C_p = 6.84 + 0.00038\,\mathrm{T}$; CH_3OH (*g*), $C_p = 6.16 + 0.0183\,\mathrm{T}$. For CH_3OH $\lambda_e = 9000$ cal.; vapour pressure $= 125$ mm. at $25°$ C.

(i) Find the heat of the reaction at $298°$ K. for gaseous components. In the reaction $CO + 2H_2 = CH_3OH$ (*l*), $\Delta Z_{298} = -44,500 - (-32,500) = -12,000$ cal. and $Q_{298} = -59,900 - (-26,150) = -33,750$ cal. But CH_3OH (*l*) $= CH_3OH$ (*g*) $+ 9000$ cal. Hence for $CO + 2H_2 = CH_3OH$ (*g*), $Q_{298} = -33,750 + 9000 = -24,750$ cal. The corresponding change in $\Delta Z =$ work obtained on evaporating 1 mol. of CH_3OH at its vapour pressure to 1 atm., less the external work equal to $\mathrm{A} = \mathrm{RT} \ln 760/125 = 1050$ cal. Hence $\Delta Z_{298} = -12,000 + 1050 = -10,950$ cal. for the gaseous reaction.

(ii) Find a relation between ΔZ and T; use (65), which may be written $Q_p/\mathrm{T}^2 = (d\mathrm{A}'/d\mathrm{T})/\mathrm{T} - \mathrm{A}'/\mathrm{T}^2$, or $-\Delta Z = \mathrm{T} \int (Q_p/\mathrm{T}^2) d\mathrm{T}$. This necessitates a knowledge of the dependence of Q_p on T. Use Kirchhoff's equation and the specific heats given, and show that $Q_p = Q_0 - 14\mathrm{T} + 0.00825\,\mathrm{T}^2$. Since $Q_p = -24,750$ when $\mathrm{T} = 298$,

$\therefore Q_0 = -21{,}300$ and $Q_p = -21{,}300 - 14\,T + 0{\cdot}00825\,T^2$. Hence $-\Delta Z / T = \int [(-21{,}300 / T^2) - 14 / T + 0{\cdot}00825]\, dT = 21{,}300 / T - 14\ \ln T + 0{\cdot}00825\,T + constant$, or $A' = 21{,}300 - 32{\cdot}2\,T\ \log T + 0{\cdot}00825\,T^2 + constant\ T^2$. Put $\Delta Z = -10{,}950$ and $T = 298^\circ$ K. and find that $constant = 42{\cdot}5$. Hence the required expression is $A' = 21{,}300 - 32{\cdot}2T\log T + 0{\cdot}00825T^2 + 42{\cdot}5T$.

3. The calculation of affinity at 25° may also be carried out with the aid of *entropy tables* or *affinity tables*. Such tables, drawn up for elements and compounds at 25° and 1 atm., will be found in Lewis and Randall, *Thermodynamics*, p. 464 and p. 607, and in MacDougall, *Thermodynamics and Chemistry* (1926), p. 389 and p. 398. In many cases the figures are more or less provisional. By combining (52) and (63) we have $\Delta Z = \Delta H - T\Delta S$ or $A' = Q + T\Delta S$. Let us calculate the affinity of the reaction 6C (graphite) $+ 3H_2 = C_6H_6$ (l) at 25°, given that the heat of this reaction is $-11{,}700$ cal. at 25°. By referring to the entropy tables it is seen that $\Delta S = 44{\cdot}5$ for C_6H_6, $29{\cdot}5$ for H_2, and $1{\cdot}27$ for graphite, whence the total $\Delta S = 44{\cdot}5 - 3 \times 29{\cdot}5 - 6 \times 1{\cdot}27 = -51{\cdot}62$. Hence $A' = -11{,}700 - 15{,}400 = -27{,}100$ *cal.* at 25°.

Again, for the reaction $CH_4 + 3O_2 = CO_2 + 2H_2O$ (g), we find from the tables the following affinities of formation at 25°: CH_4, 12,800; CO_2, 94,260; H_2O (g), 54,507, whence A' at 25° is $94{,}260 + 2 \times 54{,}507 - 12{,}800 = 190{,}474$ cal. Obviously the use of such tables enables I to be determined in (66), since they furnish a value of A' at one temperature. The tables are really dependent on Nernst's heat theorem.

EXERCISES.—X

1. The vapour pressure of pure H_2O_2 is 29 mm. at 69° and 65 mm. at 85° C. Estimate ΔF for the change H_2O_2 $(l) = H_2O_2$ (g) at 25°.

2. The entropy per g. atom of graphite is $1{\cdot}3$ cal./1° at 25° and of diamond $0{\cdot}6$ cal./1°. The heat of combustion of diamond exceeds that of graphite by 180 cal. Calculate the value of ΔZ for the conversion of graphite into diamond.

3. For a certain process ΔZ is a linear function of T; at $T = 300^\circ$ it is 40,000 cal. and at $T = 400^\circ$ it is 30,000 cal. Calculate Q_p at 100°.

4. Calculate ΔZ at 25° of I_2 at 1 atm. and of I_2 in molal solution. At 25° the vapour pressure of I_2 is $0{\cdot}305$ mm. and its solution in water $0{\cdot}00132$ molal.

5. The heat of vaporization of liquid I_2 at the m.p., 114°, is 10,500 cal./mol. The heat of sublimation at the same temperature is 14,540 cal./mol. Assuming the heat capacity of the system to be independent of temperature, show that ΔF for the reaction I_2 $(s) = I_2$ (l) is about 920 cal. at the m.p.

6. The specific volume of liquid Hg is $0{\cdot}07846$ c.c./g. at the b.p. 375° C. Calculate ΔZ attending the evaporation of 1 mol of Hg at this temperature, assuming the vapour to be a perfect gas.

7. Calculate ΔZ at 25° for the reaction: 2C (graphite) $+ 3H_2 + \frac{1}{2}O_2 = C_2H_5OH$ (l). The heat of the reaction is 66,700 cal. at 25° and the following standard entropies at 25° are obtained from tables: C_2H_5OH (l), 42·6; graphite, 1·72; H_2, 29·5; O_2, 48·2.

8. Using some of the data in Example 1, calculate ΔZ for the reaction Br_2 (l) $\longrightarrow Br_2$ (g) at 25°, given the following standard entropies: Br_2 (l), 36·8; Br_2 (g), 59·6.

9. The heat of transition of grey Sn to white Sn at 0° C. is 532 cal./g. atom (absorbed). If c_p (white) $- c_p$ (grey) $= 0·49 + 3·25 \times 10^{-8}(300 - T)^3$, deduce an expression for the heat of transition as a function of T: find the value of this heat at 80° K. and 200° K. Find also an expression for the affinity of the transition, given that the transition point ($p = 1$ atm.) is 19° C.

10. The transition point between monoclinic (β) and rhombic (α) S is 95° C. ($p = 1$ atm.). The atomic heats are: S_α, $C_p = 4·12 + 0·0047\,T$; S_β, $C_p = 3·62 + 0·0072\,T$. The heat of the transition $S_\beta \longrightarrow S_\alpha = 77$ cal./g. atom (evolved) at 0° C. Show that at 25° the rhombic form of S is the more stable. Show also that the heat of transition at 0° K. is 120 cal./g. atom.

11. The atomic heat of S_λ is $5·4 + 0·005\,T$. The heat of the transition $S_\alpha \longrightarrow S_\lambda$ is 467 cal. (evolved) at 100°, and when S_α melts to form S_λ the m.p. is 112·8° C. Using data in the previous exercise, calculate ΔZ for the change $S_\alpha \longrightarrow S_\lambda$ at 25°.

12. The heat evolved in the reaction CO (g) $+ \frac{1}{2}O_2$ (g) $= CO_2$ (g) at 18° is 68,100 cal.; the values of C_p for CO and O_2 are $6·5 + 0·001\,T$ and for CO_2, $7·0 + 0·0071\,T - 0·0_5186\,T^2$. Given that ΔZ at 298° K. is $- 61,750$ cal., find whether CO_2 is more, or less, stable at 2500° than at 18° C.

13. At 293° K. 21,730 cal. are evolved in the reaction C $+ 2H_2 = CH_4$. Given the following values of C_p: CH_4, $3·47 + 0·019\,T$; H_2, $6·52 + 0·00044\,T$; C, $1·1 + 0·0024\,T + 4·0 \times 10^{-7}T^2$, and that $\Delta Z = - 14,500$ cal. at 298° K., show that $\Delta Z = - 19,280 - 10·67\,T$ lnT $+ 0·0786\,T^2 + 0·0_76\,T^3 + 42·2\,T$.

14. The heat of the reaction $H_2 + \frac{1}{2}O_2 = H_2O$ (l) is 68,270 cal. at 25°, whilst ΔZ is $- 56,560$ at the same temperature, and the vapour pressure of H_2O is 23·8 mm. Given the following values of C_p: H_2, $6·50 + 0·0009\,T$; O_2, $6·50 + 0·001\,T$; H_2O (g), $8·81 - 0·0019\,T + 0·0_5222\,T^2$, calculate ΔZ for the formation of steam at 100°. Assume water vapour to be an ideal gas; $\lambda_e = 10,450$ cal./mol. at 25°.

<div style="text-align:center">

CHAPTER II

Characteristic Equations

</div>

<div style="text-align:center">(a) THE IDEAL GAS</div>

(1) Boyle's Law:

$$pv = \text{constant} = k_T \text{ at constant T.} \qquad (70)$$

(2) Joule's Law:

$$(\partial u / \partial v)_T = 0. \qquad (71)$$

(3) General Gas Law:

$$pV = nRT, \qquad (72)$$

in which n mols of gas occupy vol. V at temperature T under a pressure p, R being the *gas constant*. It must be carefully noted that equation (72) does *not* define an ideal gas. This is a gas which obeys (70) and (71). Equations (70) to (72) are obeyed accurately by actual gases only at very low pressures.

Units.—Since n is a number, the value of R depends on the units of p and V. If p is expressed in atm. and V in l., R is in l. atm./(mol × T); if p is in dynes/cm.^{2} and V in cm.^{3}, R is in dynes × cm./T or ergs/T. The dimensions of R are [work]/[temperature]; hence R may be expressed in work or heat units if we assume T to be dimensionless. The following values refer to 1 mol.

$$R = 0.08207 \text{ l. atm./degree} = 8.3156 \times 10^7 \text{ ergs/degree}$$
$$= 84,801 \text{ g. cm./degree} = 1.9875 \text{ g. cal./degree}$$
$$= 8.3156 \text{ joules/degree.}$$

These values depend on the adoption of the conventional centigrade scale of absolute temperatures. Useful approximations are 0.082 l. atm. and 1.99, or 2, cal.

The *normal density*, D, of a gas or vapour is the weight in g. of 1 l. measured at S.T.P., i.e. at 0° C. and under a pressure of 760 mm. of Hg also at 0° C., the weights being reduced to sea-level and latitude 45°. (N.B.—1 l. = 1000.027 c.c.) If the gas is ideal, 1 l. weighs M/22.415 g. (approx. M/22.4) at S.T.P., where M = mol. wt.

(4) Laws of Mixed Gases.

Let p, V, T be the pressure, vol., and temperature of a mixture of non-interacting gases. Let p_1, p_2, ... be the pressures (*partial pressures*) exerted by the separate gases in a vol. V at temperature T. Then (*Dalton's law*):

$$p = p_1 + p_2 + \ldots \quad \ldots \quad \ldots \quad (73)$$

Let v_1, v_2, ... be the vols. occupied by the separate gases at pressure p and temperature T. Then (*Leduc's law*):

$$v = v_1 + v_2 + \ldots \quad \ldots \quad \ldots \quad (74)$$

At higher pressures (74) is a closer approximation than (73).

EXAMPLES.—1. A faulty barometer (containing air) reads 748 mm. when the true pressure is 753 mm., and 754 mm. when the true pressure is 761 mm. Calculate the true pressure when the reading is 759 mm.
Let a = cross-section of the barometer tube. Let the amount of air present occupy a length l of the tube under a pressure of h mm. (i) True pressure = 753 mm.; hence pressure on air above the mercury = 753 − 748 = 5 mm. Hence, by (70), if x = length of " vacuum ", $5ax = hal$, or $x = hl/5$, and the length of the tube = 748 + $hl/5$ mm. (ii) When the true pressure is 761 mm., the length of the " vacuum " = 748 + $hl/5$ − 754 = ($hl/5$) − 6 mm. The pressure of the air in this length = 761 − 754 = 7 mm. Hence by (70): $7a[(hl/5) − 6] = hal$, or $hl = 105$, and length of tube = 769 mm. (iii) If l' = true height when barometer reads 759 mm., by (70): (769 − 759)(l' − 759)a = hal = 105a, or $l' = 769.5$ mm.

2. 7170 c.c. of air, reduced to S.T.P., were passed over I_2 at 80°. The air was then passed through Na_2CO_3 solution and the latter was found to give on precipitation 3·0461 g. of AgI. Calculate the vapour pressure of I_2 at 80°, the barometric pressure being 759·5 mm. (I = 126·95; Ag = 107·88.)
3·0461 g. of AgI = 3·0461 × 126·95/234·83 = 1·647 g. of I_2. Now 2 × 126·95 = 253·9 g. of I_2 occupy 22·4 l. at S.T.P. Hence 1·647 g. of I_2 occupy 22·4 × 1·647/253·9 = 0·1453 l., and the vol. of (air + I_2) = 7·3153 l. The fraction of I_2 present by vol. = 0·1453/7·3153 and so p, the pressure of the I_2 vapour = 0·1453 × 759·5/7·3153 = 15·09 mm.

3. Calculate the vapour pressure of alcohol at 24·97° from the following data. Dry air was passed over EtOH contained in bulbs immersed in a thermostat at 24·97°. After removal of EtOH vapour by P_2O_5 the vol. of the air was measured at 19·4° over water. When 8456 c.c. of air had been measured the bulbs had lost 1·3692 g. The barometric pressure, P, was 738·8 mm. The coefficient of expansion of air, α, = 0·003571 per degree and its normal density = 1·293 g./l. The vapour pressure of water at 19·4° = 16·9 mm.

If p = partial pressure of air in the bulbs at equilibrium and p_1 = that of EtOH, then $P = p + p_1$. But $pv_1 = wRT/M$, where v_1 = vol. of air + saturated EtOH vapour in the bulbs, w is the weight of air aspirated (in g.) and M = hypothetical mol. wt. of air (= $1 \cdot 293 \times 22 \cdot 4 = 28 \cdot 96$). Similarly, if w_1 = loss in weight of bulbs and M_1 = mol. wt. of EtOH vapour (= $46 \cdot 058$), $p_1 v_1 = w_1 RT/M_1$. Hence $p_1[1 + (M_1 w/M w_1)] = P = 738 \cdot 8 = p_1[1 + (46 \cdot 058\ w/39 \cdot 65)]$. The value of w is now required in order to find p_1. If p' = vapour pressure of water at $t°$, and if v = vol. of air measured, then $(P - p')v = (w/M)RT = (w/M)[760 \times 22 \cdot 4(1 + \alpha t)]$. Hence $w = (738 \cdot 8 - 16 \cdot 9) \times 8 \cdot 456 \times 28 \cdot 96/760 \times 22 \cdot 4 \times 1 \cdot 0693 = 9 \cdot 713$ g., so that $p_1 = 738 \cdot 8/[1 + (46 \cdot 058 \times 9 \cdot 713/39 \cdot 65)] = 60 \cdot 13$ mm.

4. Dry H_2 was bubbled through three saturators, the first containing EtOH, the second a $3 \cdot 188N$ solution of HCl in EtOH, and the third water. The barometer stood at 759 mm., and the water in the third vessel absorbed HCl equivalent to $59 \cdot 94$ c.c. of $0 \cdot 1N$ alkali. The loss in weight of the first vessel was $3 \cdot 443$ g., and the pressure of the gas leaving it was 779 mm., that of the gas leaving the second saturator being 770 mm. Temperature = $25°$. Given that the vapour pressure of EtOH = $59 \cdot 5$ mm. at $25°$, calculate the partial pressure of HCl over the alcoholic solution.

Fraction of EtOH vapour (by vol.) in gases leaving the first saturator = $59 \cdot 5/779$. Now $3 \cdot 443$ g. of EtOH would occupy $3 \cdot 443 \times 22,400 \times 298 \times 760/46 \times 273 \times 59 \cdot 5 = 23,370$ c.c. at $25°$ and $59 \cdot 5$ mm. Hence $23,370$ = total vol. of H_2 + EtOH leaving first saturator at 779 mm. Vol. of HCl removed from the second vessel = $22,400 \times 0 \cdot 5994 \times 0 \cdot 365 \times 760 \times 298/36 \cdot 5 \times 770 \times 273 = 144 \cdot 6$ c.c. at $25°$ and 770 mm. Hence partial pressure of HCl in second vessel = $770 \times 144 \cdot 6 \times 770/23,370 \times 779 = 4 \cdot 71$ mm.

5. The capillary of a McLeod gauge is $0 \cdot 012$ cm. in diameter. The vol. of the bulb is $121 \cdot 2$ c.c. What pressure corresponds to a gauge registration of $3 \cdot 8$ cm.?

The gauge, used for measuring very low pressures, is illustrated in fig. 4. D is attached to the low-pressure apparatus; C is attached to a barometer tube connected to a reservoir of Hg. On raising the reservoir the Hg traps at C a known vol. ($121 \cdot 2$ c.c.) of air in CBA, at an initial pressure equal to the pressure p in the apparatus. The reservoir is raised until the Hg at Y is on a level with the tip of the capillary A. The trapped air is thus compressed by pressure YX′ (= $3 \cdot 8$ cm.) to the vol. AX (= $3 \cdot 8 \times \pi \times 0 \cdot 006 \times 0 \cdot 006$). Hence, from (70) (which holds exactly under the low pressures considered): $121 \cdot 2\ p = (3 \cdot 8)^2(0 \cdot 006)^2\pi$ or $p = 0 \cdot 0000135$ cm.

Fig. 4 —Head of McLeod Gauge

1. A barometer reads 770 mm. when the true atmospheric pressure is 781 mm., and 748 mm. when the true pressure is 756 mm. Calculate the true pressure when the reading is 762 mm.

2. A defective barometer containing air registers 755 mm. when the true pressure is 765 mm. The length of the " vacuum " is 25 mm. Calculate the true pressure when the apparent value is 765 mm.

3. 0·0248 g. of $NaHCO_3$ when dropped into a bulb immersed in molten Pb (m.p. 327° C.) sets up an excess pressure of 12·5 mm. on a manometer. In the same apparatus 0·0212 g. of $CuSO_4$ crystals gave a pressure of 17·9 mm., and 0·0444 g. of $BaCl_2$ crystals 15·3 mm. Find the formulæ of the crystalline hydrates.

4. 0·0364 g. of naphthalene was completely vaporized in a bulb of 113 c.c. capacity, heated by the vapour from boiling quinoline. A pressure increase corresponding to 7·9 mm. was set up. Calculate the b.p. of quinoline.

5. 0·02 g. of $NaHCO_3$, when introduced into a constant-vol. apparatus kept at 300° C., gives rise by its complete decomposition to a pressure increase of 98 mm. of Hg. Calculate the vol. of the apparatus. (Lond. B.Sc. Hons., 1924.)

6. 3 l. of dry air, measured at 15° and 755 mm., were passed over C_2H_5OH at 30°. The latter lost 0·5964 g. in weight. Calculate the vapour pressure of alcohol at 30°.

7. Find the value of R when the Fahrenheit degree is adopted for the absolute scale.

8. Show that $pV = RT$ does not define the ideal gas.

9. The vapour pressure of I_2 at 137° is 200 mm. What vol. of air, measured at 20° and 763 mm., would have to be passed over 10 g. of I_2 at 137° to produce complete sublimation?

10. The vol. of the bulb of a McLeod gauge is 55·7 c.c. (C to B in fig. 4). The capillary has a diameter of 0·0172 cm. What pressure corresponds to a reading of 1·73 cm.?

11. What pressure corresponds to a reading of 4·29 cm. on a M'Leod gauge having a bulb of vol. 78·9 c.c. and a capillary of diameter 0·011 cm.?

12. The reservoir of a McLeod gauge attached to an exhausted vessel was raised until the air trapped in the bulb (81·2 c.c.) was compressed to a length of 9 cm. in a capillary of radius 0·012 cm. The Hg column X'Y (fig. 4) was 6·42 cm. Calculate the pressure in the exhausted vessel.

(5) Limiting Densities.

Extrapolation of the (pv, p) curve for a mass W of gas to $p = 0$ gives $(pv)_0$, which is finite. If the gas occupies v l. at 0°

and p atm., the normal density, D, is $W/(pv)_1$, the subscript referring to $p = 1$ atm. The *limiting density* is

$$D_0 = W/(pv)_0 = D_1[(pv)_1/(pv)_0]. \quad . \quad . \quad (75)$$

At very low pressures Avogadro's law applies *exactly*; hence for two gases A and B, the ratio of the molecular weights is

$$M_A/M_B = (D_0)_A/(D_0)_B, \quad . \quad . \quad . \quad (76)$$

or, with O_2 as standard ($M = 32$; $D_0 = 1.42762$),

$$M = 32 D_0/1.42762 = 22.4149 D_0. \quad . \quad (76a)$$

For gases deviating only slightly from (70), $[(pv)_0 - (pv)]/(pv)_0 = \lambda p$, where λ is a constant for each gas at $0°$, the *compressibility coefficient* λ may be determined from two measurements of pv below 1 atm., or from Berthelot's equation, according to which, for 1 mol.,

$$T \; 2\lambda \; \neg$$

$$\text{;ay,} \quad (77)$$

where $A = f(p)$; $(pv)_0 = RT$ (because $A_0 = 1$), and $(pv)_1 = A_1 RT$. Hence

$$D_0 = D_1 A_1 = D_1(1 - \lambda_1). \quad . \quad . \quad (78)$$

Note that λ_1 is usually written as λ.

At a temperature such that $T^2 = 6T_c^2$, $A = 1$ and the gas (although not ideal) obeys Boyle's law (*Boyle point*). In the case of more compressible gases $(pv)_0$ is found by extrapolation of pv to $p = 0$.

EXAMPLES.—1. The normal density of O_2 is 1.42898 g./l. and its compressibility coefficient 0.00097. For C_2H_4 the normal density is 1.26057 and the compressibility coefficient 0.00790. If the atomic weight of H_2 is 1.0078, calculate the atomic weight of C.

According to (78), $(D_0)_{O_2} = D_1(1 - \lambda) = 1.42898(1 - 0.00097)$ = 1.42759. Similarly, $(D_0)_{C_2H_4} = 1.26057(1 - 0.0079) = 1.25061$. Hence (mol. wt. C_2H_4)/(mol. wt. O_2) = 1.25061/1.42759 = 0.876028; ∴ mol. wt. C_2H_4 = 0.876028 × 32 = 28.0329, and atomic weight of C = (28.0329 − 4 × 1.0078)/2 = *12.0008*.

2. The density of SO_2 is 2.9266 g./l. at $0°$ and 1 atm. and 1.4460 at $0°$ and 1/2 atm. If the ideal mol. vol. is 22.415 l. at S.T.P., calculate the at. wt. of S.

Now $[(pv)_0 - (pv)] = \lambda(pv)_0 p$, or $pv = (pv)_0 + Bp$, where B is a constant. Refer all quantities to 2.9266 g. of gas. This occupies 1 l.

at $0°$ and 1 atm. and $2·9266/1·4460$ l. at $0°$ and $1/2$ atm. Hence $1 = (pv)_0 + B$ and $2·9266/2 \times 1·4460 = (pv)_0 + B/2$, from which $B = - 0·02392$ and $(pv)_0 = 1·02392$; $\therefore$ $D_0 = 2·9266/1·02392 = 2·85823$ and $M = 22·415 D_0 = 64·067$, giving at. wt. of $S = 64·067 - 32 = 32·067$.

EXERCISES.—XII

(Seven-figure logs are necessary for some of these exercises.)

1. The compressibility coefficient of N_2O is $+ 0·00747$; its normal density is $1·9777$ g./l. The compressibility coefficient of O_2 is $0·00097$, and its atomic weight $16·000$. Calculate the atomic weight of N.

2. From the following densities, D, and compressibility coefficients, λ, calculate the atomic weight of Br_2 ($O = 16$):

		H_2	O_2	HBr
D	..	0·089873	1·42898	3·6440
λ	..	$- 0·00054$	$+ 0·00097$	$+ 0·00929$

3. Calculate the atomic weight of N given at. wt. of $H = 1·0078$, density of $NH_3 = 0·7708$, pc for $NH_3 = 112·3$ atm., Tc for $NH_3 = 406°$ K. Ideal mol. vol. $= 22·415$ l.

4. The values of pv/RT per mol of SO_2 at $0°$ C. are $0·9973$ when $p = 0·1$ atm. and $0·9759$ when $p = 1$ atm. The density of SO_2 at S.T.P. is $2·9266$ g./l. Find the atomic weight of S ($O = 16$).

5. The volume of a quantity of O_2 at $0°$ C. was measured at $607·97$ and $204·30$ mm. pressure; the corresponding pv products (in arbitrary units) were found to be $56,267$ and $56,296$ respectively. Assuming that $d(pv)/dp$ is constant between the pressure limits 0 and 1 atm., and that the normal density of O_2 is $1·42900$, calculate the limiting density. (Manc. Hons. Chem., 1920.)

6. The density of Ne is $0·44986$ at $0°$ and $0·5$ atm. and $0·9002$ at $0°$ and 1 atm. Assuming the ideal mol. vol. to be $22·415$, calculate the mol. wt. of Ne.

7. Calculate the atomic weight of C, given that the density of CO is $1·2504$ and that of O_2, $1·42900$, the compressibility coefficients being $+ 0·00081$ and $+ 0·00094$ respectively ($O = 16$).

8. Calculate the atomic weight of Cl ($H = 1·008$) from the following values of p and v for HCl gas at $0°$:

p (mm.)	829·5	604·71	515·35	384·13	223·95	157·57
v (c.c.)	66·012	90·815	106·642	143·259	246·119	349·978

The normal density of HCl is $1·63915$ g./l., and the limiting density of O_2, $1·42762$.

9. The weight of 1 l. of SO_2 at $0°$ under different pressures is as follows:

w (g.)	..	2·9266	2·1817	1·9802	1·44572	1·1820
p (mm.)	..	760	570	518·2	380	311·3

Calculate graphically the compressibility coefficient.

10. If T_c for CH_3Cl is $416\cdot3°$ K. and p_c is $65\cdot85$ atm., the normal density being $2\cdot30450$ g./l., calculate the mol. wt.   Assume ideal mol. vol. $= 22\cdot415$ l.

(b) Van der Waals' Equation

(1) Van der Waals' Equation.

This equation is

$$(p + n^2a/v^2)(v - nb) = n\mathrm{R}T, \qquad . \quad . \quad (79)$$

where a and b are constants for a given substance and v is the volume of n mols. The equation should apply both to liquids and gases.

Units.—a/v^2 is a pressure ("internal pressure"); hence $a = pressure \times (vol.)^2$. b is a vol. (the "co-volume" $= 4$ times the space actually occupied by the molecules). The values of a and b given in the present book refer to 1 mol of gas. If p is expressed in atm. and v in l., a must be in atm. $\times$ l.^{2}, b in l., and R in l. atm./T ($= 0\cdot08207$).

Other units are used but are not recommended. If v_0 is the mol. vol. of a substance at 0° and 1 atm., then on dividing (79) throughout by nv_0, we have (equation 79a): $(p + a'/v_1{}^2)$ $(v_1 - b') = \mathrm{R}'T$, where v_1 is the vol. of the substance expressed as a fraction of the normal (mol.) vol. at 0° and 1 atm. Hence $a' = a/v_0{}^2$, $b' = b/v_0$, and $\mathrm{R}' = \mathrm{R}/v_0 = 1/273$. Since when $p = 1$ atm. and $T = 273$, $v_1 = 1$, this equation may be written (79b): $(p + a'/v_1{}^2)(v_1 - b') = (1 + a')(1 - b')T/273$. Other writers refer v_0 and v_1 to 1 g. of substance instead of 1 mol. If $a' = \alpha a$, $b' = \beta b$, $\mathrm{R}' = \gamma \mathrm{R}$, then (with the units of a and b in c.c., atm., and mol) the following relations hold good.

Unit of Volume.	Unit of Press.	Unit of Mass.	a	β	γ
c.c.	atm.	mol	1	1	1
c.c.	mm.	mol	760	1	760
lit.	atm.	mol	1×10^{-6}	1×10^{-3}	1×10^{-3}
lit.	mm.	mol	76×10^{-5}	1×10^{-3}	76×10^{-2}
c.c.	atm.	gm.	M^{-2}	M^{-1}	M^{-1}
c.c. per g. at S.T.P.	atm.	—	*$1\cdot993 \times 10^{-9}$ $\times M^{-2}$	$4\cdot465 \times 10^{-5}$ $\times M^{-1}$	$4\cdot465 \times 10^{-5}$ $\times M^{-1}$
c.c. per mol at S.T.P.	atm.	—	$1\cdot993 \times 10^{-9}$	$4\cdot465 \times 10^{-5}$	$4\cdot465 \times 10^{-5}$

* $1\cdot993 \times 10^{-9} = (4\cdot465 \times 10^{-5})^2 = (22,400)^{-2}$.

Sometimes the equation is given in terms of the coefficient of expansion of an ideal gas, α $(= 1/273)$: $(p + a'/v_1{}^2)(v_1 - b')$ $= (1 + a')(1 - b')(1 + \alpha t) = R''(1 + \alpha t)$ $[= R'T]$. The value R'' is then usually quoted for R, but is not the general gas constant of (72).

Illustration.—For CO_2, $a = 3 \cdot 6 \times 10^6$ and $b = 42 \cdot 8$ (c.c.; mol; atm.). If the equation is to be used with v expressed as a fraction of the mol. vol. at $0°$ and 1 atm., then $a' = 3 \cdot 6 \times 10^6 \times 1 \cdot 993 \times 10^{-9} = 0 \cdot 00717$ and $b' = 42 \cdot 8 \times 4 \cdot 465 \times 10^{-5} = 0 \cdot 001915$. If a' and b' are required in terms of the specific volume as unit of vol., then these values must be divided by M^2 and M, respectively, giving $0 \cdot 0000371$ and $0 \cdot 0000435$. In terms of the units c.c., atm., g. the values are 1860 and $0 \cdot 974$.

(2) Critical Constants.

Equation (79), written as a cubic in v, has 3 roots which are equal at the critical point, whence:

$$v_c = 3b; \quad p_c = a/27b^2; \quad T_c = 8a/27Rb. \quad . \quad (80)$$

By expressing v, p, and T as functions of v_c, p_c, and T_c, so that

$$v = \varphi v_c; \quad p = \pi p_c; \quad T = \theta T, \quad . \quad . \quad (81)$$

and substituting in (79), we have

$$\text{)} - 1) = 8\theta, \quad . \quad . \quad . \quad (82)$$

an equation which contains no characteristic constants (*reduced equation*), and which should be true, therefore, for any mass of any substance. This is only approximately the case in actual fact. Substances in states characterized by the same values of π, φ, and θ are said to be in *corresponding states*.

Units.—Express a, b, and R in terms of atm., c.c., mol, then, in (80), v_c is in c.c., p_c in atm., and T_c in °K. If a' and b' are referred to 1 mol of substance (in the gaseous state) at $0°$ and 1 atm., then v_c is in terms of the mol. vol. at $0°$ and 1 atm. as unity and must be multiplied by $22 \cdot 4$ for conversion to litres. p_c is obtained in atm. as before; in accordance with (79b), however, the expression for T_c becomes $8a'/27b' \cdot 273/(1 + a')(1 - b')$.

Illustration.—For CO_2, $a = 3 \cdot 6 \times 10^6$ and $b = 42 \cdot 8$ (c.c.;

atm.; mol). Hence $T_c = 8 \times 3.6 \times 10^6/27 \times 82.07 \times 42.8$ $= 303.7°$ K. and $p_c = 3.6 \times 10^6/27 \times 42.8 \times 42.8 = 72.8$ atm. Now in terms of mol. vol. (c.c.) at S.T.P. $a' = 0.00717$ and $b' = 0.001915$. Hence $v_c = 3 \times 0.001915 \times 22,400 =$ 128.6 c.c., the previous units giving $3 \times 42.8 = 128.4$ c.c. Also, $T_c = 8 \times 0.00717 \times 273/27 \times 0.001915 \times 1.00717 \times$ $0.998085 = 301.5°$ K., and $p_c = 0.00717/27 \times 0.001915 \times$ $0.001915 = 72.4$ atm. The slight differences are due to the approximate value (22.4 instead of 22.415) assumed for the mol. vol.

EXAMPLE.—Calculate the mol. vol. of CO_2 at $60°$ and 25 atm. if the van der Waals' constants are $a = 3.6 \times 10^6$ atm. $\times$ c.c.^{2} and $b = 42.8$ c.c.

If v is the required volume in c.c., then from (79): $[25 + (3.6 \times 10^6)/v^2](v - 42.8) = RT = 82.07 \times 333$, or $25 v^3 - 28,399.3 v^2 + 3.6 \times 10^6 v - 154.08 \times 10^6 = 0$. This equation may be solved by Newton's method; a simple calculation involving the gas laws shows that $v = 1100$ approx. Now $f(1100) = 2717.72 \times 10^6$ and $f'(1100) = 31.87 \times 10^6$; $f(1100)/f'(1100) = 85.3$ approx., so that the second approximation is $1100 - 85.3 = 1014.7$. A repetition of the process gives $f(1014.7) = 377.24 \times 10^6$ and $f'(1014.7) = 23.2 \times 10^6$; $f(1014.7)/f'(1014.7) = 16.3$. The third approximation is 998.4. We have $f(998.4) = 11.86 \times 10^6$ and $f'(998.4) = 21.7 \times 10^6$; $f(998.4)/f'(998.4) = 0.55$. The fourth approximation is thus $998.4 - 0.55 = 997.85$. Using this value we have $f(997.85) = + 0.02 \times 10^6$ and $f'(997.85) = 21.6 \times 10^6$, so that the next correction is of the order 10^{-9}. The required volume, therefore, is *997.85 c.c.* It should be noted that $f(997.85)$, if 997.85 is the correct solution, should be zero, whereas actually it is 2×10^4. This is because a very small change in v causes a very large change in $f(v)$; thus $f(997.84) = - 26.5 \times 10^4$, so that the exact solution is between 997.85 and 997.84 and is nearer the former figure. The accuracy of (79) does not warrant the calculation of v to more than the nearest c.c.

Difficulties with regard to the units of a and b may often be surmounted by using (82). Thus, for CO_2 $p_c = 72.8$ atm., $v_c = 128.6$ c.c./mol, and $T_c = 303.7°$ K., whence, for the above example, $\pi = 25/72.8 = 0.3434$, $\theta = 333/303.7 = 1.099$, and $\varphi = v/128.6$. Then $[0.3434 + 3(128.6/v)^2][3v/128.6 - 1] = 8 \times 1.099$ or $0.0080109 v^3 - 9.1354 v^2 + 1157.4 v - 49,614 = 0$, i.e. $25 v^3 - 28,509.3 v^2 + 3.61 \times 10^6 v - 154.8 \times 10^6 = 0$. The slight difference between this equation and the one deduced previously is due to approximate values of p_c, v_c, and T_c.

EXERCISES. XIII

1. For Cl_2, $a = 5.34 \times 10^6$ atm. $\times$ (c.c.)^2 and $b = 46$ c.c./mol. Calculate the pressure of Cl_2 at $50°$ C. when 2 mols of the gas occupy 30 l.

2. Calculate b for the following substances:

	(i) H_2	(ii) NH_3	(iii) H_2S	(iv) Et_2O	(v) Cl_2
T_c (°K.) ..	33·2	406·0	373·4	466·9	417·0
p_c (atm.) ..	12·8	112·3	89·1	35·6	76·1

3. For H_2, $T_c = 33\cdot18°$ K. and $p_c = 12\cdot80$ atm. Calculate a and b, and find at what temperature 8 g. of H_2 occupy 100 l. under a pressure of 1 atm.

4. For CO_2, $a = 3\cdot609 \times 10^6$ and $b = 42\cdot75$ (c.c., atm., mol). Calculate p_c and T_c.

5. From data given in Exercise 2 above calculate the diameters of the H_2 and Cl_2 molecules ($N_0 = 6\cdot06 \times 10^{23}$).

6. The density of argon is 1·7838 g./l.; $p_c = 52\cdot9$ atm. and $T_c = 155\cdot6°$ K. Estimate the mol. wt.

7. For a gas obeying (79),

$$C_p - C_v = R + 2a/vT = R + 2ap/RT^2. \quad . \quad . \quad (83)$$

For Cl_2 at 18° C., $C_p = 8\cdot06$ cal./1°. If $a = 5\cdot34 \times 10^6$ atm. $\times$ (c.c.)^2, calculate C_v. (Obs. value = 5·96 cal./1°.)

8. For H_2O, $a = 5\cdot47 \times 10^6$ and $b = 30\cdot55$ (c.c., atm., mol). Calculate the mol. vol. of water vapour at 25° and 1 atm.

9. Calculate the value of b (in c.c. per mol) for He at 0°, given that $pv = 1$ when $p = 1$ atm. and 1·0139 when $p = 26\cdot634$ atm. [Hint: The temperature is not too low, and the pressure is fairly small, so that the vol. per mol is large and van der Waals' equation may be simplified].

10. The value of b for fluorobenzene is 128·5 c.c./mol. If the Avogadro constant is $6\cdot06 \times 10^{23}$, calculate the mean diameter of the fluorobenzene molecule.

11. For N_2O, $p_c = 71\cdot65$ atm. and $T_c = 309\cdot5°$ K. The normal density at S.T.P. is 1·9777 g./l. Calculate the mol. wt. of the gas.

(3) Joule-Thomson Effect.

The temperature change caused by the expansion of a gas through a porous plug is given by ($C.\ T.$, § 43):

$$. \ \partial(v/T)_p/\partial T. \quad . \quad . \quad (84)$$

For a gas obeying (79),

$$- b)/C_p \quad . \quad . \quad (85)$$

approx., where T_1 is the initial temperature. The effect changes sign when $T_1 = 2a/Rb$ (*inversion temperature*; the *Boyle point* is $T_1' = a/Rb$). In (85) if p is in atm., a in atm./c.c.^{2}, b in c.c., then R and C_p are in c.c. atm.

EXAMPLE.—Calculate the fall in temperature produced by allowing O_2 at 2 atm. and 0° to pass through a porous plug into a space in which the pressure is 1 atm., given that $a = 1\cdot332 \times 10^6$ atm. $\times$ c.c.^{2}, $b = 31\cdot18$ c.c./mol, and $C_p = 6\cdot9$ cal./mol/1°.

Use (85). $C_p = 6\cdot9$ cal. $= 6\cdot9 \times 41\cdot29$ c.c. atm. R $= 82\cdot07$ c.c. atm. $\Delta p = 2 - 1 = 1$ atm. $\therefore \Delta T = (2\cdot664 \times 10^6/82\cdot07 \times 273 - 31\cdot18)/6\cdot9 \times 41\cdot29 = -0\cdot32°$. The *fall* in temperature is 0·32°.

EXERCISES.—XIV

1. Calculate the fall in temperature produced by allowing N_2 at 5 atm. and 10° C. to pass adiabatically through a porous plug into a space in which the pressure is 0·5 atm., given that $a = 1\cdot345 \times 10^6$ atm. $\times$ c.c.^{2}, $b = 39\cdot6$ c.c./mol, and $C_v = 4\cdot9$ cal./mol/1°.

2. Calculate the inversion temperature for H_2, for which gas $a = 0\cdot244 \times 10^6$ atm. $\times$ c.c.^{2} and $b = 26\cdot70$ c.c./mol.

3. A more accurate expression for the Joule-Thomson effect is

$$dT/dp = [2a/RT - 3abp/R^2T^2 - b]/C_p. \quad . \quad . \quad (86)$$

The plot of T against p for the expression within the brackets equated to zero is called the *inversion curve* for the substance. Plot the curve for ether, given $a = 17\cdot44 \times 10^6$ atm. $\times$ c.c.^{2} and $b = 134\cdot7$ c.c. Above what value of p will there be heating on expansion?

4. The critical temperature of NH_3 is 406° K. Calculate the Boyle point.

(c) FUGACITY

(1) Definition and Calculation.

The *fugacity* of a substance, f, is defined by the equation

$$Z = RT \ln f + constant, \quad . \quad . \quad . \quad (87)$$

where *constant* is a function of T only. Between two isothermal states, (87) becomes

$$Z_B - Z_A = RT \ln f_B/f_A. \quad . \quad . \quad . \quad (88)$$

The fugacity of a substance represents an " ideal " or " corrected " vapour pressure; it equals the vapour pressure when the vapour is a perfect gas. The perfect gas is usually regarded as the standard state. For an actual gas the difference between f and p is a measure of the divergence of the gas from the ideal state. The fugacity of a substance in each of two phases in equilibrium is the same. Equations (87) and (88) apply to the ideal gas when the concentration is substituted for the fugacity.

The following examples illustrate fugacity calculations.*

* Lewis and Randall, *Thermodynamics*, p. 190.

EXAMPLES.—1. Calculate the fugacity of CO_2 at 200 atm. from Amagat's results at 50°:

p (atm.) ..	1	50	100	125	200	400	600
pv/RT ..	1	0·920	0·491	0·395	0·500	0·8515	1·1865

From (63), $dZ = dU - TdS - SdT + pdV + Vdp = Vdp - SdT$ and $(\partial Z/\partial p)_T = V$. By (87) this becomes $(\partial \ln f/\partial p)_T = V/RT$, or $RT \ln f/f' = \int_{p'}^{p} V dp$. Plot p against V from the figures given; plot on the same graph $pV = RT = 1$, the latter value being chosen arbitrarily to agree with the unit of the experimental figures. Draw the ordinate at $p = 200$ atm. Now, as $p' \longrightarrow 0$, $p' \longrightarrow f'$. Hence, if A is the area bounded by the two curves to infinite volume and the ordinate, $RT \ln f = RT \ln p - A = RT \ln 200 - A$, where f refers to 200 atm. By counting the squares $A = 0.7$ l. atm. approx. Hence $\ln f = \ln 200 - 0.7$ or $\log f = 2.3010 - 0.3043 = 1.9967$ or $f = 99.1\ atm.$

A better graphical method is the following. The mol. vol. according to (72) is RT/p; if the observed mol. vol. is V, then, if $\alpha = RT/p - V$, we have $RT d \ln f = V dp = RT dp/p - \alpha dp$, or

$$= RT \ln p - \int_{0}^{p} \alpha dp. \quad \text{The same expression holds when V}$$

is the volume of any number of mols. To solve the problem plot α against p. Then the area under the curve between $p = 0$ and $p = 200$ is obviously equal to the quantity A above. By counting the squares we find $A = 0.744$ l. atm., whence (since $RT = 1$) $f = 94.5\ atm.$, a more accurate value than the preceding one. Care must be taken to give the areas the correct sign in these graphical methods.

2. Calculate the fugacity of CO_2 at 50° and 200 atm. if the van der Waals' constants are $a = 3.6 \times 10^6$, $b = 42.8$ (c.c., atm., mol).

Substituting for dp in the equation $RT \ln f/f' = \int_{p'}^{p}$, with the aid of van der Waals' equation we have, on integration (as $p' \longrightarrow 0$, $V' - b \longrightarrow V'$; $1/V' \longrightarrow 0$; $V' \longrightarrow RT/p'$, and $p' \longrightarrow f'$):

$$\ln f = \ln RT/(V - b) + b/(V - b) - 2a/RTV. \quad . \quad (89)$$

First calculate V for $p = 200$ atm. and $T = 323°$ (cf. p. 48); $V = 73.21$ c.c., approx. Hence $\log f = \log 82.07 \times 323/30.4 + 42.8/2.3 \times 30.4 - 7.2 \times 10^6/82.07 \times 323 \times 73.2 \times 2.3 = 2.9405 + 0.6120 - 1.6110$, or $f = 87.4\ atm.$

3. Calculate approximately the fugacity of CO_2 at 60° and 25 atm., given that the mol. vol. under these conditions is 1008·5 c.c.

At constant temperature and very low pressure the difference between the actual volume of a gas and the ideal volume is a constant. Hence, $RT \ln f/f' = \int_{p'}^{p} V dp = \int_{p'}^{p} (RT/p - \alpha) dp = RT \ln p/p' - \alpha(p - p')$, whence, when $p' \longrightarrow 0$ and $p' = f'$,

$$fP = p^2, \quad . \quad . \quad . \quad . \quad . \quad (90)$$

where P is the pressure an ideal gas would exert in the given volume. (90), which is the *Lewis and Randall fugacity rule*, is usually valid up to several atm. In the present case, $P = 82 \cdot 07 \times 333/1008 \cdot 5$ and $p = 25$ atm. Hence $f = 25 \times 25 \times 1008 \cdot 5 / 82 \cdot 07 \times 333 = 23 \cdot 1$ *atm.*

CHAPTER III

Liquids and Solutions

(1) Surface Energy of Liquids.

The *molar surface energy* of a liquid is $\sigma(Mv)^{2/3}$, where v is the specific volume, and σ the surface tension. According to *Eötvös' law* for unassociated liquids:

$$d[\sigma(Mv)^{2/3}]/dT = -k, \quad . \quad . \quad . \quad (91)$$

where, according to Ramsay and Shields, $k = 2 \cdot 12$ ergs/1°, approx., independent of the nature of the liquid (σ in dynes/cm. or ergs/cm.²). Variations of k from this value indicate that the law of corresponding states is not obeyed; the cause for this is assumed to be association. The degree of association, x, cannot safely be calculated from the deviation of k from the normal value, although the equation

$$\sigma_1(Mx\,v_1)^{2/3} - \sigma_2(Mx\,v_2)^{2/3} = k(T_2 - T_1) \quad (91a)$$

is commonly used for this purpose. Ramsay and Shields found (92) to be more accurate than (91) when $T_c - T$ exceeds 35°:

$$\sigma(Mv)^{2/3} = k(T_c - T - 6). \quad . \quad . \quad (92)$$

The *surface tension* of a liquid which rises to a height h in a capillary tube of radius r is

$$\sigma = \tfrac{1}{2}gr(d - d')(h + r/3)\sec\alpha, \quad . \quad . \quad (93)$$

where $g = 981$ cm./sec.², and d, d' are the densities of the liquid and vapour respectively. d' may often be neglected. For liquids which wet the glass $\sec\alpha = 1$.

The *parachor*, P, of a compound is defined as $M\sigma^{0 \cdot 25}/(d_l - d_g) =$ (at low temperatures) *mol. vol.* $\times \sigma^{0 \cdot 25}$. To within 3 per cent $P = 0 \cdot 78\,v_c$.

(2) **Adsorption.**—Adsorption is change of concentration at an interface; when the solute increases in concentration the adsorption is positive. Adsorption is usually represented by an empirical isotherm (Freundlich),

$$x/m = ac^{1/n}, \quad \cdots \cdots \quad (94)$$

where m is the mass of adsorbent, $x =$ amount of substance absorbed at equilibrium, and $c =$ equilibrium concentration of solution; a and n are constants. *Gibbs's adsorption equation* is

$$(c/RT)(d\sigma/dc) = -\Gamma \quad \cdots \quad (95)$$

where Γ is the *adsorption excess* at unit surface, i.e. the difference in concentration (in mols) at the surface and in the solution per unit area.

EXAMPLE.—Calculate the surface excess in g. mol./sq. cm. in the surface layers of a solution of butyric acid, $0.3N$, given that the surface tension is 49.8 dynes/cm. for a concentration of 0.2675 g. mol./l. and 43.6 dynes/cm. at 0.4353 g. mol./l.; $T = 290°$ K. Assume that the change in σ with concentration is linear. (Lond. B.Sc. Hons., 1927.)

If $\sigma = a + bc$, where c is the concentration, $b = d\sigma / dc = -6.2/0.1678$ (dynes/cm.)/(g. mol./l.). Also $R = 8.3 \times 10^7$ ergs/mol. Hence $-\Gamma = -(6.2/0.1678)(0.3/8.3 \times 10^7 \times 290)$ or $\Gamma = 4.6 \times 10^{-10}$ *mol/cm.*^{2}

EXERCISES.—XV

1. The heights, h cm., to which n-octane rises in a capillary tube of $r = 0.01425$ cm., at different temperatures, $t°$ C., are ($d =$ density):

t	..	15·5	46·3	78·3
h	..	4·32	3·91	3·445
d	..	0·7058	0·6803	0·6534

Calculate σ at each of these temperatures. Is the liquid associated?

2. The surface tension of isocapronic acid, $Me_2CH.CH_2.CH_2 COOH$, was measured at different temperatures, $t°$ C., by noting the rise, h cm., of the liquid in a capillary tube of $r = 0.012935$ cm.

t	..	17·0	46·5	78·2	132·3
h	..	4·53	4·14	3·83	3·28
d	..	0·9239	0·8995	0·8714	0·8245

Calculate the surface tension at each temperature. What is the apparent mol. wt. of the acid between 78° and 132°?

3. The surface tension of H_2O_2 is 75.94 dynes/cm. at $18.2°$ and

78·73 dynes/cm. at 0·2°.   The densities at these temperatures are 1·4434 and 1·4630, respectively. What is the degree of association?

4. The corrected height to which C_6H_5Cl will rise in a capillary ($r = 0·012935$ cm.) at 150° is 1·484 cm. Calculate T_c if the density of the liquid is 0·9599 and that of the vapour 0·0054 g./cm³.

5. Liquid C_2H_6 rises 2·20 cm. in a capillary of $r = 0·0272$ cm. at −88·1° C. The density of the liquid at this temperature, d_l, is 0·5457, and that of the vapour over the liquid, d_g, 0·0020. Calculate σ, and also the mol. surface energy.

6. For liquid HI, σ $= 72·13 − 0·1911T$ dynes/cm. Calculate the Eötvös constant over the range − 48° C. to −37° C., given that the density is related to the temperature by $d = 2·799 [1 + 0·0043(237·4 − T)]$.

7. Calculate the surface excess in g. mol./cm.² in the surface layers of a solution of diethyl malonate, 0·10105 molal, given that σ is 43·685 dynes/cm. for a concentration of 0·1344 M and 51·115 dynes/cm. for a concentration of 0·0677 M. T $= 293°$ K.

8. The following figures refer to the adsorption of MeCOOH in water by charcoal at 25°:

Equil. conc. (mol./l.)	0·018	0·0616	0·126	0·208	0·882
y	0·467	0·801	1·11	1·55	2·48

where $y =$ amount adsorbed by unit mass of charcoal. Show that the adsorption isotherm holds. (Plot $\log y$ against $\log c$.)

9. For a solution containing 0·002 g. of Na glycocholate (M $= 140$) per cubic centimetre, $d\sigma/dc = −4750$ dynes/(g./c.c.). If T $= 289°$ K. calculate the adsorption excess (g./cm.³) in the surface layers of the solution.

(a) DILUTE SOLUTIONS

(1) Osmotic Pressure.

P, the *osmotic pressure* (O.P.) of a dilute solution is given by (van't Hoff, 1887)

$$Pv = nRT, \quad \ldots \ldots (96)$$

where n mols of solute are contained in a volume v of solution. For *units* see p. 40. More accurate results are obtained if v is taken as the volume of solvent (Morse and Frazer).

In the case of electrolytes equation (96) may be written

$$Pv = inRT, \quad (96a)$$

where i is *van't Hoff's factor*. If each mol of solute, dissociated to the extent x, gives ν ions, then $i = 1 + (ν − 1)x$.

EXERCISES.—XVI

1. The O.P. of a cane-sugar solution containing 1 mol of sugar in 1000 g. of H_2O (equivalent to 0·825 mol of sugar per litre of solution) is 26·62 atm. at 20°. Compare this figure with the calculated values obtained by applying (96) in the manner of van't Hoff and of Morse and Frazer.

2. A $0·01N$ solution of HCl is dissociated to an extent 0·972 at 0°. Calculate the O.P.

3. In a solution containing 14·87 g. of KBr per litre the salt is 82 per cent dissociated at 25°. Calculate the O.P.

4. The O.P. of a $0·5N$ solution of NaCl is 20·29 atm. at 18° C. Calculate the degree of dissociation of the salt.

5. The Ostwald absorption coefficient (p. 84) for CO_2 in Me acetate at 100 mm. and −78° is 224·3. Calculate the O.P. of the solution at this temperature.

(2) Vapour Pressure. Raoult's Law.

The *vapour pressure*, p, of a dilute solution of n mols of a non-volatile solute in an amount of volatile solvent which would produce N mols of vapour is, if p_0 is the vapour pressure of the pure solvent, given by

$$\ln(p_0/p) = n/N. \quad \ldots \quad (97)$$

$$\therefore (p_0 - p)/p_0 = n/(N + n) = N_2 \text{ approx.} \quad (98)$$

In very dilute solutions

$$(p_0 - p)/p_0 = n/N. \quad \ldots \quad (99)$$

If the relative molal lowering of vapour pressure, $(p_0 - p)/p_0 M = \Delta$, for various solutions is plotted against the molality M, then Δ is independent of T (*Babo's law*), so that all the observations plot on the same graph (Leopold and Johnston, 1927). The method is very sensitive.

The O.P. of a solution of specific gravity s and concentration c (mol/l.) is

$$P = RT/M_0 \cdot (s - c \cdot ds/dc) \ln(p_0/p), \quad . \quad (100)$$

where $M_0 =$ mol. wt. of gaseous solvent. For very dilute solutions $s = s_0$, $c = 0$:

$$P = RTs_0/M_0 \cdot \ln p_0/p = (p_0 - p)RTs_0/M_0 p. \quad (101)$$

If s is in g./cm.^{3}, R in c.c. atm./1° (= 82·1), P is in atm.

EXERCISES.—XVII

1. Calculate the mol. wt. of glycerol in a solution of 21·24 g. in 100 g. of water, if the vapour pressure of the solution is 4·432 mm. at 0° and that of water 4·620 mm.

2. A solution of Ca ferrocyanide containing 313·9 g. in 1000 g. of water has a vapour pressure of 4·434 mm. at 0°. Calculate the O.P. of the solution if the vapour pressure of water at 0° is 4·580 mm.

3. The density of a 5 per cent solution of NaCl at 18° is 1·0345. Calculate the vapour pressure of the solution at 18°. The vapour pressure of pure water at this temperature is 15·33 mm., and the NaCl in the solution is dissociated to the extent of 69·7 per cent. (Lond. B.Sc. Hons., 1925.)

4. A solution of 0·855 g. of a metal in 100 g. of Hg had, at a given temperature, a vapour pressure of 752·6 mm., that of pure Hg at the same temperature being 758 mm. Using (98), calculate the mol. wt. of the metal, taking that of Hg as 200. (Lond. B.Sc. Hons. (Ex.), 1911.)

5. The vapour pressure of water at 0° is lowered by 0·02321 mm. by the solution of 9·31 g. of KOH in 1000 g. Calculate the van't Hoff factor i for the solution. Vapour pressure H_2O at 0° = 4·580 mm.

6. The vapour pressure of pure water is 17·4736 mm. at 19·94° and that of a solution of 0·0979 mol of KNO_3 in 1000 g. of water is 17·4191 mm. Calculate the osmotic pressure of the solution and the degree of dissociation of the salt.

7. A solution of 1·509 mols of Ca ferrocyanide in 1 l. of water has a density of 1·322 at 0° which increases by 0·180 per unit increase in concentration. The ratio vapour pressure of solution/vapour pressure of water = 1·107. Calculate the O.P. of the solution.

8. A solution of 1·323 mols of Ca ferrocyanide in 1 l. of water has an O.P. of 87·35 atm. The density of the solution is 1·287, increasing by 0·188 per unit increase in concentration. The vapour pressure of water at 0° is 4·580 mm.; calculate the vapour pressure of the solution. Calculate also the degree of dissociation.

(3) Boiling-point.

The elevation of b.p., ΔT, of W g. of solvent (density d) when w g. of a non-volatile solute is dissolved in it is:

$$\Delta T = Bn/(N + n) = B N_2 \quad . \quad . \quad . \quad (102)$$

$$= E \cdot \frac{w/M}{W/1000} = E' \cdot \frac{w/M}{W/100} = E'' \cdot \frac{w/M}{W/100d}. \quad (103)$$

E, E', and E'' are values of the *molecular elevation of b.p.*

referred to 1 mol of solute in 1000 g., 100 g., or 100 c.c. of solvent, respectively.

$$E = RT_0^2/1000\,L_e \quad . \quad . \quad . \quad . \quad (104)$$

where $T_0 = $ b.p. and $L_e = $ latent heat of evaporation of the solvent.

$$P = d \,.\, L_e \,\Delta T/T_0. \qquad . \quad . \quad . \quad (105)$$

If d is in g./c.c., L_e in cal./g., P is in cal./cm.³ Since 1 cal. = 41·29 atm. cm.³, the right-hand side of (105) multiplied by 41·29 gives P in atm.

EXAMPLES.—1. A solution of a binary salt of mol. wt. 74·5, containing 0·520 g. of salt in 100 g. of water, boils at 99·815°, the boiling temperature of the water being 99·757°. If the molecular elevation constant of water is 0·52 (per 1000 g. of solvent), calculate the degree of dissociation of the salt.

The vapour pressure of the solution at the boiling temperature is 753·400 mm. and that of the solvent 754·973 mm. The density of the solution is 0·9588 at the same temperature. Calculate the osmotic pressure.

Let M′ be the apparent mol. wt. Then $0·520 \times 10/M'$ mol. of salt are dissolved in 1000 g. of water. Hence $0·058 = \Delta T = E \times 5·2/M' = 0·52 \times 5·2/M'$ or M′ = 46·62. If x is the degree of dissociation then 1 mol of salt gives rise to $(1 + x)$ g. ions. The weight of salt in 1000 g. of water = 5·2 g. The number of dissolved g. molecules and ions in 1000 g. of water = $5·2(1 + x)/74·5$. Hence M′ = $46·62 = 5·2 \times 74·5/5·2(1 + x)$, or $x = 0·598$. On substituting in (101) we have: P = $1·573 \times 82·1 \times 372·8 \times 0·9588/18 \times 753·4 = 3·40$ atm.

2. Calculate the mol. wt. of I_2 in CCl_4 if 10·4 g. of I_2 raise the b.p. of 1000 g. of CCl_4 by 0·135°; $E = 4·8$ per 1000 g. A solution of 2·163 g. of I_2 in 100 g. of CCl_4 on distillation left a solution of 2·532 g. of I_2 in 100 g. of CCl_4 and gave a distillate weighing 13·804 g. and containing 0·123 g. of I_2.

The application of the b.p. method to the case of a *volatile solute* depends on the experimental fact that during the initial stages of the distillation the ratio of the concentrations of solute in the vapour (= distillate) and solution is a constant, α. In the present case, mean concentration of liquid = $\frac{1}{2}(2·163 + 2·532) = 2·348$ per 100 g. and concentration of distillate = $0·123/13·681 = 0·899$ per 100 g.; hence $\alpha = 0·899/2·348 = 0·38$.

Let $\Delta\tau$ be the elevation in b.p. which would have been observed had the solute been non-volatile. Then a combination of (104) and (41) gives: $1000E = pM\,dt/dp$, where M is the mol. wt. of the solvent and p its vapour pressure at the b.p. Also, (103) gives $E = m\,\Delta\tau/10·4$, where m is the required mol. wt. Now if $p_1 = $ partial pressure of solute and p_2 that of solvent in the vapour at the b.p., $p_1/p_2 = Mc/$

1000 m, where c is the concentration of solute ($=$ g./1000 g. of solvent) in the vapour, or $p_1 = 0.38 \times 10.4\, p_2 M / 1000 m$. Equating the two expressions for E, and, as a close approximation, putting $dp = p_1$ and $p_2 = p$, the vapour pressure of the pure solvent at the b.p., we have $dt = 0.38\, \Delta\tau$, or $\Delta\tau = (\Delta\tau - dt)/(1 - 0.38)$. But $\Delta\tau - dt =$ observed b.p. elevation, ΔT. Hence $\Delta T = 0.62\, \Delta\tau$ or $\Delta\tau = 0.218$ and $m = 10.4 \times 4.8/0.218 = 233$.

EXERCISES.—XVIII

1. What can be said with regard to the state of S in CS_2 solution from the following data?

(i) g. of $CS_2 = 17.79$ g. of S $= 0.2096$ b.p. $= 46.307°$

(ii) „ „ $= 19.18$ „ $= 0.2170$ „ $= 46.304°$

The b.p. of CS_2 is $46.2°$ and the molecular elevation is 2.37 per 1000 g.

2. The b.p. of 100 g. of aniline was raised $0.154°$ by the solution of 0.976 g. of benzil (Ph.CO.CO.Ph). Calculate the latent heat of evaporation of aniline (b.p. $184°$).

3. An aqueous solution of $Ba(NO_2)_2$, containing 110.7 g./l., boils at $100.46°$ C. Calculate the degree of dissociation of the salt. (Ba $= 137.4$; L_e for water $= 536$ cal./g.). (Lond. B.Sc. Hons., 1925.)

4. A solution containing 0.5 g. of a substance of mol. wt. 182 dissolved in 42 g. of C_6H_6 boils at $80.175°$ C. The b.p. of C_6H_6 is $80.000°$ C. What is its latent heat of evaporation? (Lond. B.Sc. Hons., 1922.)

5. For SO_2, $L_e = 92.45$ cal./g. at the b.p., $263°$ K. Calculate the mol. wt. of acetanilide if a solution of 1.555 g. in 14.7 c.c. of liquid SO_2 raises the b.p. of the latter $0.79°$. The density of liquid SO_2 is 1.460 g./c.c. at $-10°$ C.

6. A solution of KCl containing 3.291 g. of salt in 100 g. of water boils at $99.972°$, the boiling temperature of the water being $99.586°$. If the molecular elevation constant is 0.52 per 1000 g., calculate the degree of dissociation of the KCl. If the vapour pressure of the water is 759.24 mm. at $99.586°$ and if the barometric pressure was 748.80 mm. when the temperature of the boiling solution was read, calculate the O.P. of the solution at $100°$ C. The density of the solution is 0.9590 at the b.p.

7. Calculate the mol. wt. of I_2 in C_6H_6 if 8.762 g. of I_2 in 100 g. of C_6H_6 raise the b.p. of the latter $0.680°$; $E' = 26.7$ per 100 g. A solution of 2.347 g. of I_2 in 100 g. of C_6H_6 on distillation left a solution containing 2.967 g. of I_2 in 100 g. of C_6H_6 and gave a distillate weighing 20.66 g. and containing 0.165 g. of I_2.

8. A solution of 5.572 g. of I_2 in 100 g. of methylal on distillation gave a distillate weighing 6.852 g. and containing 0.041 g. of I_2. The residual liquid contained 6.484 g. of I_2 per 100 g. of methylal. Calculate the mol. wt. of I_2 in this solvent if a solution of 1.955 g. of I_2 in 100 g. raises the b.p. $0.173°$. $E' = 21$ per 100 g.

9. The b.p. of C_6H_6 is raised $0.403°$ by the solution of 2.47 g. of

Et benzoate in 100 g. The density of C_6H_6 at the b.p. is (
$L_e = 94.4$ cal./g. What is the O.P. of the solution?

(4) Freezing-point.

The depression of f.p., when pure solid solvent separates, is
given by equations similar to those used for elevation of b.p.
(see p. 56):

$$\Delta T = D \cdot n/(N + n) = D_{N_2} \quad . \quad . \quad (106)$$

$$= G \cdot \frac{w/M}{W/1000} = G' \cdot \frac{w/M}{W/100} \quad . \quad (107)$$

where G, G' are the molecular depressions of f.p. for 1 mol of
solute in 1000 g. or 100 g., respectively, of solvent. The rela-
tion between f.p. T_0 and vapour pressure is:

$$\ln p_0/p = n/N = \lambda_f \cdot \Delta T/RTT_0$$
$$= \lambda_f \Delta T/RT_0^2 \text{ approx.} \quad . \quad . \quad (108)$$

When $n = 1$, $N = 1000/M_0$, then $\Delta T = G$

$$\therefore G = RT_0^2/1000 L_f ; \quad . \quad . \quad (109)$$

also: $$P = d \cdot L_f \Delta T/T_0. \quad . \quad . \quad . \quad (110)$$

For aqueous solutions an accurate equation is:

$$P(\text{atm.}) = 12.06 \Delta T(1 - 0.0026 \Delta T). \quad (111)$$

EXAMPLES.—1. A solution of 0.4660 g. of NaCl in 1 l. of water
has a f.p. of $-0.0291°$. The depression constant of the solvent is
1.858 (per. 1000 g.), its heat of fusion is 79.74 cal./g. at the m.p.,
and its vapour pressure 4.58 mm. at the same temperature. Calculate
the degree of dissociation of the salt in the solution and the vapour
pressure of the solution.

Let M' be the apparent mol. wt. Now 1000 g. of water contain
$0.4660/M'$ mol. of NaCl. Hence $0.0291 = 1.858 \times 0.4660/M'$ or
$M' = 29.75$. If x is the degree of dissociation, then 1 mol of NaCl
gives $(1 + x)$ g. ions, so that 1000 g. of solvent, which contain 0.1168
g. of salt, also contain $0.4660(1 + x)/58.5$ dissolved mol; hence,
$29.75 = 58.5/(1 + x)$ or $x = 0.966$.
Substitution in (108) gives $2.3 \log 4.58/p = 18 \times 79.74/1.985(273)^2$,
whence $p = 4.54$ mm.

2. The vapour pressure of ice at $-4°$ is 3.277 mm. What is the
vapour pressure of supercooled water at the same temperature?
$L_f = 79.74$ cal./g. for ice at $0°$.

Since the vapour pressure, p, of a solution at its f.p., T, equals that of the pure solid solvent at the same temperature, then (108) gives a relation between p and p_0, the vapour pressure of the pure solvent (supercooled) at T. Hence $\ln p_0/3 \cdot 277 = 79 \cdot 74 \times 18 \times 4/1 \cdot 985 \times (269)^2$ or $p_0 = 3 \cdot 410$ mm.

EXERCISES.—XIX

1. Calculate the degrees of dissociation, x, of the following substances in the given aqueous solutions ($G = 1 \cdot 858$ per 1000 g.). Weight of solvent $= 1000$ g.

Substance.	Weight of Substance (g.).	F.p. Depression.	x
K_2SO_4	0·17433	0·0054	(i)
$BaCl_2$	0·8293	0·0209	(ii)
NH_4OH	0·2394	0·0142	(iii)
HNO_3	6·675	0·3735	(iv)
Na_2CO_3	0·02401 (mol.)	0·1285	(v)

2. Given that the formula of hydrogen peroxide is $(HO)_x$, calculate the value of x from the following f.p. experiments on aqueous hydrogen peroxide solutions. Assume $G = 1 \cdot 86$ per 1000 g.

Weight of Solution.	Weight of $(HO)_x$ Present.	F.p. °C.
16·48	0·0207	— 0·069
18·84	0·0509	— 0·151
17·79	0·1834	— 0·571
17·84	0·2634	— 0·805

3. To 15·401 g. of C_6H_6, f.p. 5·400°, 3·747 g. of a C_6H_6 solution of P saturated at 18° were added. The f.p. of the mixture was 5·155°. Assuming P to exist in C_6H_6 solution as P_4, and taking the molecular depression as 5·00 per 1000 g., calculate the percentage solubility of P in C_6H_6 at 18°.

4. A $2N$ $Ba(NO_2)_2$ solution containing 11·474 g. of salt in 46·546 g. of water freezes at $- 3 \cdot 931°$. The density of the solution is 1·161 at 0°; the heat of fusion of water is 79·74 cal./g. and its vapour pressure 4·58 mm., both at the m.p. The latent heat of evaporation of water at 100° is 539 cal./g. Calculate: (i) the degree of dissociation of the salt; (ii) the vapour pressure of the solution at the f.p.; (iii) the O.P. of the solution at the f.p., and (iv) the b.p. of the solution. (N.B.—No additional data to be assumed.)

5. The latent heat of fusion of $HgCl_2$ is 16·9 cal./g. at the m.p., 264·5° C. A solution of 0·2976 g. of Hg_2Cl_2 in 50 g. of $HgCl_2$ depressed the f.p. of the la tter by 0·430°. Calculate the mol. wt. of Hg_2Cl_2 in $HgCl_2$ solution.

6. A solution of 1·632 g. of $CCl_3.COOH$ in 100 g. of C_6H_6 had a f.p. 0·350° lower than that of pure C_6H_6. The molecular depression for C_6H_6 is 5·0 per 1000 g. What can be said regarding the state of this acid in C_6H_6 solution?

7. The f.p. of a 0·5052 molal cane sugar solution is − 0·9892°. If the vapour pressure of water at this temperature is 4·255 mm. and the heat of fusion of ice is 1438 cal./mol at the m.p., calculate the vapour pressure of the solution.

8. A 0·004278 molal solution of cane sugar freezes at − 0·007957°. Calculate the O.P. of the solution in atm. if L_f for H_2O is 79·65 cal./g.

9. The f.p. of $SnCl_4$ (− 30·45°) is depressed 0·135° on saturation with C_2H_2. Show that the solubility of the latter is 0·0253 g./100 g. of liquid. $L_f = 8·42$ cal./g.

10. A solution contains 85·5 g. of sucrose/1000 g. of water and is also N/100 with respect to HCl. Calculate as nearly as possible the f.p.: (i) of the freshly prepared solution; (ii) of the solution after half of the sucrose has been inverted. Mol. depression for 1 Kg. of water = 1·858°. (Lond. B.Sc. Hons., 1924.)

11. The addition of 0·1407 g. of mesitylene (C_9H_{12}) to 11·375 g. of palmitic acid ($C_{16}H_{32}O_2$) lowered the f.p. of the latter from 62·25° C. to 61·81° C. Find the latent heat of fusion per g. of palmitic acid. (Lond. B.Sc. Special, 1927.)

12. The association factor of phenol in a 2·94 per cent (by weight) bromoform solution is 1·71. If the mol. f.p. depression for this solvent is 141 and its f.p. 7·60°, calculate the f.p. of the solution. Calculate also the depression constant per 100 c.c. of solvent, if its d is 2·901 at the f.p.

13. Naphthalene and diphenylamine form a eutectic at 32·45°. A solution of 1·268 g. of eutectic in 18·43 g. of naphthalene depresses the f.p. of the latter 1·890°. If the mol. depression of naphthalene is 67·8 per 100 g., calculate the composition of the eutectic.

14. A more accurate form of (108) is

$$\ln \frac{p_0}{p} = \frac{1}{R}\left[\frac{\lambda_f}{T_0}\cdot\frac{\Delta T}{T} - \frac{a}{2}\left(\frac{\Delta T}{T}\right)^2 + \frac{a}{3}\left(\frac{\Delta T}{T}\right)^3\right], \qquad (112)$$

where λ_f is the heat of fusion of the solvent at T and a is the difference between the mol. heats of the liquid and solid solvent (= 9·07 cal. for water).*

Calculate the vapour pressure of a KCl solution of f.p.− 0·175°. The vapour pressure of water at 0° is 4·620 mm. and $\lambda_f = 1435·5$.

15. The vapour pressure of ice at − 11° is 1·780 mm. What is that of supercooled water at the same temperature? L_f for ice = 79·74 cal. at 0°.

* It is often assumed that $\ln p_0/p$ is independent of T, so that (112) may be used to calculate p at other temperatures by using the appropriate value of p

(b) ACTIVITY

(1) Activity in Solution (Non-Electrolytes).

The difference between the partial molal thermodynamic potentials of a solute at two concentrations is

$$\bar{z} - \bar{z}_0 = RT \ln f/f_0, \quad . \quad . \quad . \quad (113)$$

or $d\bar{z} = RT \, d \ln f$. If f_0 refers to some arbitrary standard state, f/f_0 is the (relative) *activity*, a; if the standard state is such that $\bar{z}_0 = 0$ and $f_0 = 1$, then (114) $\bar{z} = RT \ln a$, and

$$\Delta z = RT \ln a_2/a_1 = RT \ln f_2/f_1. \quad . \quad (115)$$

For a *gas* the standard state is chosen for which $f = 1$ ($a = f$ or $a/p = 1$ when $p = 0$); for a *solvent*, the activity of the pure solvent is taken as unity (a_1/N_1, when $N_1 = 1$); whilst for a *solute*, the activity in the standard state is equal to the molality M at infinite dilution ($a_2/M_2 = 1$ when $M_2 = 0$; or $a_2/N_2 = 1$ when $N_2 = 0$).

Equation (114) may be substituted in (6),

$$\log \frac{a_1}{N_1} - \log \frac{a_1'}{N_1'} = - \int_{N_2'}^{N_2} \frac{N_2}{N_1} d \log \frac{a_2}{N_2}, \quad (116)$$

enabling the activity a_1 of one component of a solution to be calculated when that of the other component is known.

Equation (116) is readily integrated graphically between two compositions N_2, N_2'. If one of these compositions is taken as infinite dilution, $N_2' = 0$, then $a_1'/N_1' = 1$ and

$$\log \frac{a_1}{N_1} = - \int_0^{N_2} \frac{N_2}{N_1} d \log \frac{a_2}{N_2}. \quad . \quad . \quad (117)$$

The corresponding equation for a_2 is unsuitable for graphical computation.

The activity of the water at the f.p. of an aqueous solution of a non-electrolyte, molality M, is $\log a_1 = - 0.004211 \Delta T - 0.0_5 22 (\Delta T)^2$, where ΔT is the f.p. depression of the solvent. Assuming a_1 to be independent of T for a given concentration, a_2 may be calculated with the aid of (6), the final equation being

$$\ln \frac{a_2}{M} = - \int_0^M \frac{j}{M} dM + \int_0^M 0.00057 \frac{(\Delta T)}{M} d(\Delta T) - j, \quad (118)$$

where $j = 1 - (\Delta T)/1.858\,M$. The first definite integral is the area under the plot of j/M against M, and the second integral (which is only significant at higher concentrations, e.g. $3M$) is 0.00057 times the area under the graph of $\Delta T/M$ against ΔT.

A simple *empirical rule* for not too concentrated solutions is:

$$2.303 \log a_2/M = -2j. \quad . \quad . \quad (119)$$

In using (119) j/M is plotted against M, and values of j corresponding to values of M are read off and substituted in (119).

(2) Activity Coefficients in Electrolyte Solutions.

Consider an electrolyte in M molal solution dissociating into $\nu = \nu_+ + \nu_-$ ions. Then from the law of mass action, in which the concentrations are replaced by activities, $a_+{}^{\nu+} a_-{}^{\nu-}/a_2 = K$. If the standard state is so chosen that $K = 1$, then $a_+{}^{\nu+} a_-{}^{\nu-} = a_2$, and (i) the geometric mean of the activities,* $a_\pm$, $= (a_2)^{1/\nu}$. The *activity coefficient* ("*thermodynamic degree of dissociation*") of the electrolyte is defined as

$$\gamma = a_\pm /M(\nu_+{}^{\nu+} \nu_-{}^{\nu-})^{1/\nu} = a_\pm /M_\pm, \quad . \quad (120)$$

where $M_\pm$ is the *mean molality* of the ions. The (mean) *activity coefficient* is $\gamma_\pm = \gamma = (\gamma_+{}^{\nu+} \gamma_-{}^{\nu-})^{1/\nu}$. γ may be calculated by various methods.

Calculation from f.p. measurements.—If each mol of solute yields ν ions on dissociation in dilute solution, then from (i) we find (ii), $d \ln a_\pm = d \ln (a_2)^{1/\nu} = 1/\nu \cdot d \ln a_2$. Assume †

$$d \ln a_2 = d(\Delta T)/1.858M + 0.00057 \Delta T \cdot d(\Delta T)/M. \quad (121)$$

Neglect the last term; $\therefore$ (iii) $d \ln a_\pm = d(\Delta T)/1.858\nu M$. Define j as $1 - \Delta T/1.858\nu M$; differentiate: $dj = -d(\Delta T)/1.858\nu M$. Combine with (120) and (iii);

$$\therefore d \ln \gamma = -dj - j\, d \ln M, \quad . \quad . \quad (122)$$

which may be integrated graphically if j is known as a function

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* It is usual to consider $a_+ = a_-$.

† Randall and Vanselow, *J. Amer. Chem. Soc.*, 1924, **46**, 2418.

of M. For all salts below $0.01M$, $j = \beta M^\alpha$, β and α being constants, and hence

$$\log \gamma = -\beta(\alpha + 1)M^\alpha/2.303\,\alpha = -lM^\alpha, \quad (123)$$

where l is a constant for a given electrolyte. In more concentrated solutions (up to $3M$) the equation (q = constant)

$$\log \gamma = qM - lM^\alpha \quad . \quad . \quad . \quad (124)$$

is more accurate. The constants are determined by plotting $\log [(-\log \gamma)/M + q]$ against $\log M$ for arbitrary values of q until a straight line is obtained. This line has a slope of $(\alpha - 1)$ and an intercept of $\log l$.

For uni-univalent salts $\alpha = 0.5$ approx.; hence

$$\ln \gamma = -3j \text{ or } \gamma = 1 - 3j. \quad . \quad . \quad (125)$$

In concentrated solutions the equation (cf. 118)

$$\log \gamma = -\int_0^M j\, d\log M + \frac{0.00025}{\nu}\int_0^{\Delta T}\frac{(\Delta T)}{M}d(\Delta T) - j/2.303 \quad (126)$$

holds. Since thermal effects have been neglected, (126) may safely be applied only at concentrations below $0.2\ M$. The second term is negligible below $0.1\ M$.

Osmotic Pressure, &c.—By combining (120) and (124) with (6), the following equation is obtained for the activity of water, a_1, in an electrolyte solution:

$$-\partial \ln a_1 = \nu M(2.303\,q\partial M - 2.303\,l\alpha M^{\alpha-1}\partial M + \partial \ln M)/55.5$$

or $\qquad \log a_1 = -0.004211\Delta T - 0.0_522\,(\Delta T)^2.$

Since a_1 is proportional to p, the vapour pressure of the solution, then

$$\ln p_0/p = [\nu + 2.303\,q\nu M/2 - 2.303\,l\nu\alpha M^\alpha/(\alpha + 1)]\,M/55.5. \quad (127)$$

The term within the square brackets is van't Hoff's factor, i. If v_0 is the molal vol. of the solvent, the osmotic pressure of the solution, P, is given by

$$P = RT\,Mi/55.5\,v_0, \quad . \quad . \quad . \quad (128)$$

which for aqueous solutions at $25°$ becomes: P (atm.) $= 24.42\ Mi$

These equations offer an approximate method of calculating the activity coefficients of electrolytes from a knowledge of the degree of dissociation: $x = (i - 1)/(\nu - 1) = 1 + 2\cdot3\,qvM/ 2(\nu - 1) - 2\cdot303\,l\nu\alpha M^{\alpha}/(\alpha + 1)\,(\nu - 1) = 1 + \alpha''M - \beta''M^{\alpha}$. This may be written $\log(1 - x + \alpha''M) = \log\beta'' + \alpha\log M$, which is a linear equation in $\log M$ and $\log(1 - x + \alpha''M)$. Curves are drawn for various arbitrary values of α'' until a straight line is obtained, from which the other constants are determined. γ is then calculated from (124).

Space does not permit the illustration of all the various methods of calculating activity coefficients. The few numerical examples which follow are based mainly on data in Lewis and Randall, *Thermodynamics*, p. 259 *et seq.*, to which the reader is referred. Several calculations are given in Taylor, *Physical Chemistry*, Vol. II, pp. 734 ff.

EXAMPLES.—1. The vapour pressure of Hg over an amalgam of 3·207 g. of Tl in 16·10 g. of Hg is 332·94 mm. at 323°, the vapour pressure of pure Hg being: $\log p$ (mm.) $= 9\cdot9073436 - 3276\cdot628/T - 0\cdot6519904\log T$. Assuming Hg vapour to be a perfect gas, calculate the activity of Hg in the amalgam.

The activity of the pure solvent is taken as unity. The activity of the solvent in the solution, $a_1, = f_1/f_1^0$, and if p_1 is the vapour pressure of the solvent in the solution and p_1^0 the vapour pressure of the pure solvent, then, since the gas laws are obeyed, $p_1 = f_1$ and $p_1^0 = f_1^0$, and hence $a_1 = p_1/p_1^0$. In the present example $p_1 = 332\cdot94$ mm. and $p_1^0 = 414\cdot6$, whence $p_1/p_1^0 = 0\cdot803 = a_1$.

2. The activity, a_2, of Tl in its amalgams at 20° is:

N_2 ..	0·003259	0·01675	0·04856	0·0986	0·1680	0·2074	0·2701
a_2 ..	0·003396	0·02062	0·08624	0·2772	0·7259	1·061	1·674

Calculate the activity of Hg in the amalgam containing the mol fraction 0·2 of Tl.

In accordance with (117) plot N_2/N_1 against $\log a_2/N_2$. When $N_2 = 0\cdot2$, $N_2/N_1 = 0\cdot25$. Draw the ordinate at $N_2/N_1 = 0\cdot25$ and determine the area between this ordinate, the graph, and the $\log a_2/N_2$ axis. Its negative value is $\log a_1/N_1$. Thus $a_1/N_1 = 0\cdot866$ and $a_1 = 0\cdot866 \times 0\cdot8 = 0\cdot693$.

3. The following figures give the f.p. depressions for aqueous TlCl solutions of molality M:

$M \times 10^4$ ..	19·73	29·64	36·79	44·38	16·02	19·90	30·41	37·65	47·54	59·45
$\Delta T \times 10^3$ ..	7·235	10·83	13·42	16·14	5·88	7·29	11·10	13·72	17·28	21·55

Calculate the activity coefficient of TlCl in 0·01M solution. Calculate also the activity of the water in this solution.

At 0·01M and below we may write $j = 1 - (\Delta T)/1\cdot858\,\nu M =$

βM^{α}, or $\log j = \alpha \log M + \log \beta$. Plot $\log j$ against $\log M$ ($\nu = 2$) and draw the best straight line through the points. The slope of this line gives $\alpha = 0.5$, and the intercept $\beta = 0.316$. Hence from (123), $\log \gamma = -0.316\,(1.5)\,(0.01)^{0.5}/2.303 \times 0.5$, whence $\gamma = 0.9095$. The activity of the water is given by (p. 64): $\log a_1 = -0.004211 \Delta T - 0.0_5 22\,(\Delta T)^2$. Now $\log j = 0.5 \log 0.01 + \log 0.316 = \bar{2}.5$ or $j = 0.0316 = 1 - \Delta T/3.716 \times 0.01$ or $\Delta T = 0.03599$. Hence $\log a_1 = -0.0001516 - 0.0_8 285 = -0.0001516 = \bar{1}.99985$, or $a_1 = 0.99952$.

4. The f.p. depressions of M molal HCl solutions, ΔT, are given by:

$M \times 10^3$	$\Delta T \times 10^3$	j	$\Delta T/M$
1·474	5·421	0·01044	3·677
3·430	12·53	0·01662	3·652
6·879	24·945	0·02411	3·626
17·38	62·11	0·03832	3·574
27·44	97·46	0·04414	3·552
44·01	155·7	0·04816	3·537
67·07	236·4	0·05147	3·524
104·6	368·4	0·05218	3·522
156·4	550·2	0·05119	3·526

Calculate the activity coefficient, γ, of HCl in $0.15M$ solution.

Equation (126) must be used, since M exceeds 0.01. First evaluate the integral $-\int_0^M j d\log M$. This may be divided into two parts, viz. $-\int_0^{0.01} j d\log M$ and $-\int_{0.01}^M j d\log M$. In the first integral, $j = \beta M^{\mathrm{x}}$. Hence the required integral is $-\beta(0.01)^{\alpha}/2.303\alpha - \int_{0.01}^M j d\log M$. An artifice of this kind is necessary since j cannot be measured experimentally down to zero concentrations. Determine α and β as in the previous example*; $\alpha = 0.515$, $\beta = 0.311$. Now plot j against $\log M$ and compute the area under the curve between $\log M = -2$ and $\log M = -0.824$ (i.e. $M = 0.15$). It is -0.05305. Hence $-\int_0^M j d\log M = -0.02447 - 0.05305 = -0.07752$. From the graph $j = 0.0515$ at $\log M = -0.824$; hence $\Delta T = 0.5287$ at this concentration. The integral $\int_0^{\Delta T} \Delta T/M.d(\Delta T)$ is the area under the curve of $\Delta T/M$ against ΔT. The ΔT limits in this case are 0 and 0.5287. The integral is computed to be 1.876. Hence $\log \gamma = -0.07752 + 0.000125 \times 1.876 - 0.0515/2.303 = -0.099645$ or $\gamma = 0.795$.

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* $\log j$ is a linear function of $\log M$ only up to $0.01M$.

CHAPTER IV

Equilibrium

(a) CHEMICAL EQUILIBRIUM

(1) Law of Mass Action.

Consider the isothermal, reversible gas reaction: $n_1 G_1 + n_2 G_2 + \ldots \rightleftharpoons n_1' G_1' + n_2' G_2' + \ldots$. Let the equilibrium concentrations be $[G_1], [G_2], \ldots, [G_1'], [G_2'] \ldots$. Then the *equilibrium constant* is

$$\mathrm{K}_c = \mathrm{K} = [G_1']^{n_1'} [G_2']^{n_2'} \ldots / [G_1]^{n_1} [G_2]^{n_2} \ldots, \quad (129)$$

or
$$\ln \mathrm{K} = \Sigma n_1 \ln [G_1]. \quad \ldots \quad (129a)$$

For a given temperature and a given reaction K is a constant (*Law of Mass Action*). Its numerical value depends only on the unit of concentration adopted (T = constant). The unit mol/l. is usually adopted, though when $n_1 + n_2 + \ldots = n_1' + n_2' + \ldots$ (i.e. $\Delta v = 0$) the value of K is independent of the volume unit. Some writers (e.g. Nernst) define the equilibrium constant as the reciprocal of K: $K = 1/\mathrm{K}$.

Concentrations of *solids* taking part in an equilibrium are to be omitted from (129).

Partial pressures may also be used: K is then written K' or K_p and:

$$\mathrm{K}' = p_{G_1'}^{n_1'} \times p_{G_2'}^{n_2'} \times \ldots / p_{G_1}^{n_1} \times p_{G_2}^{n_2} \times \ldots, \quad (130)$$

$$\mathrm{K}' = \mathrm{K}(\mathrm{R}T)^{n_1' + n_2' + \ldots - n_1 - n_2 - \ldots}. \quad \ldots (131)$$

If p is in atm., R = 0·082 l. atm.

EXAMPLES.—1. 4·5 g. of PCl_5 were completely vaporized at 250°, the vapour occupying 1·7 l. at 1 atm. Calculate the degree of dissociation at this temperature. Find also the total pressure which is developed when the heating takes place in a closed vessel containing 1·7 l. of Cl_2 at 25° and 1 atm.

For PCl_5, M = 208 approx.; hence number of mols of solid = 4·5/208 = 0·02163. If x = degree of dissociation ($PCl_5 \rightleftharpoons PCl_3 + Cl_2$), each mol of PCl_5 gives rise to $1 - x + x + x = 1 + x$ mols of vapour. Hence 0·02163$(1 + x)$ mols of vapour are present. From (72): 0·02163$(1 + x) = 1 \times 1\cdot7/0\cdot082 \times 523$, or $x = 0\cdot832$.

In solving the second part, (72) is applied after calculating the number of mols of gaseous product present. First find $K = [PCl_3]$ $[Cl_2]/[PCl_5]$. If a = weight of PCl_5, $[PCl_5] = a(1-x)/Mv$; $[Cl_2]$ $= [PCl_3] = ax/Mv$, and $K = ax^2/Mv(1-x) = 4.5(0.832)^2/208 \times 1.7 \times 0.168 = 0.05244$. Let β = degree of dissociation of PCl_5 at $25°$ in the Cl_2. The number of mols of latter $= pv/RT = 1 \times 1.7/0.082 \times 298 = 0.06956$. The number of mols of Cl_2 due to $PCl_5 = a\beta/M = 4.5 \beta/208 = 0.02163 \beta$. Hence $[Cl_2] = (0.06956 + 0.02163 \beta)/1.7 = 0.04093 + 0.01273 \beta$. Also $[PCl_3] = a\beta/Mv = 4.5 \beta/208 \times 1.7 = 0.01273 \beta$; $[PCl_5] = a(1-\beta)/Mv = 0.01273(1-\beta)$. Hence $K = 0.05244 = (0.01273 \beta)(0.04093 + 0.01273 \beta)/0.01273(1-\beta)$ or $\beta = 0.524$. The total number of mols present $= [0.06956 + 0.02163 (0.524)] + 0.02163(0.524) + 0.02163(1-0.524) = 0.1026$. Hence required pressure $= nRT/v = 0.1026 \times 0.082 \times 523/1.7 = 2.59\ atm.$

2. At $494°$ nitrogen dioxide is dissociated to the extent of 56.5 per cent, the pressure being 742.5 mm. Calculate K_p and K_c. Express p in atm. and c in mol/l. At what pressure will the dissociation be 80 per cent at this temperature?

Total pressure $= 742.5/760 = 0.977$ atm. If x = degree of dissociation per mol $(2NO_2 = 2NO + O_2)$, then for every initial $2NO_2$ there are $2(1-x) + 2x + x = 2 + x$ mols. Hence $p_{NO_2} = 0.977$ $(2-2x)/(2+x)$; $p_{NO} = 0.977(2x)/(2+x)$, $p_{O_2} = 0.977(x)/(2+x)$, and $K_p = p^2_{NO}p_{O_2}/p^2_{NO_2} = 0.977 \times x^3/(2+x)(1-x)^2 = 0.363$.

If p is the pressure when $x = 0.8$, then $0.363 = p(0.8)^3/(2.8)(0.2)^2$ or $p = 0.0794\ atm.$

Also $K_c = [NO]^2[O_2]/[NO_2]^2$. From (72), $c = p/RT$. Hence, $[NO_2] = p_{NO_2}/RT = 0.977(2-2x)/(2+x)RT$; $[NO] = 0.977(2x)/(2+x)RT$; and $[O_2] = 0.977(x)/(2+x)RT$. Hence $K_c = K_p/RT = 0.363/0.082 \times 767 = 0.00577.$

3. The thermal decomposition of $MnSO_4$ proceeds according to the equations: $3MnSO_4 \rightleftharpoons Mn_3O_4 + 2SO_3 + SO_2$; $2SO_3 \rightleftharpoons 2SO_2 + O_2$. The equilibrium constant, K_c, of the second reaction is given by $\log [SO_2]^2[O_2]/[SO_3]^2 = -10,373/T - 2.222 \log T + 14.585$. The total pressure set up on heating $MnSO_4$ at $1303°$ K. is 788 mm. Calculate the partial pressure of the SO_2.

Let x = amount of SO_3 in the vapour. The composition of the equilibrium gas is thus $xSO_3 + (2-x)SO_2 + (1+x/2)O_2 + SO_2$. Hence, if P is the total pressure, $p_{SO_3} = xP/[x + (2-x) + (1-x/2) + 1] = 2Px/(8-x)$; $p_{SO_2} = 2P(3-x)/(8-x)$ and $p_{O_2} = P(2-x)/(8-x)$. Now 1 g. mol. of SO_2 occupies 22.4 l. at $0°$ and 760 mm.; under a pressure of p_{SO_2} and at T the vol. is $22.4 \times 760T/273\ p_{SO_2}$, so that $[SO_2] = 273\ p_{SO_2}/760 \times 22.4T$. Similar expressions hold for $[SO_3]$ and $[O_2]$ and thence, by substitution, $K_p = K_c \times 22.4 \times 760T/273$. Hence, $K_p = p^2_{SO_2} \times p_{O_2}/p^2_{SO_3} = (3-x)^2(2-x)P/(8-x)x^2 = 760 \times 22.4TK_c/273$. Putting P $= 778$ and $K_c = 0.503$ (obtained by putting $T = 1303$ in the expression given) we find, on solving by Newton's method, that $x = 0.1872$. Hence, $p_{SO_2} = 2 \times 778(3-x)/(8-x) = 560.2\ mm.$

EQUILIBRIUM

EXERCISES.—XX

1. Water vapour at 2257° K. and 1 atm. is dissociated 1·77 per cent. Calculate the values of K_p and K_c and the partial pressures of the constituents.

2. 2·94 mols of I_2 were heated at 717° K. with 8·10 mols of H_2 in a sealed vessel; 2·83 mols of the I_2 reacted to form HI. The pressure was 1 atm. Calculate the degree of dissociation of HI at this temperature. Show that the dissociation is independent of the volume of the gas and find the partial pressure of H_2 in the vessel when the volume is increased ten-fold.
   How many g. of I_2 must be added to 1 mol of HI in order that the degree of dissociation of the latter will be 5 per cent at 717° K.?

3. The density of N_2O_4 at 49·7° and under a pressure of 93·75 mm. is 1·788 (air = 1). Show that $\alpha = 0.778$. What is the value of K_p? At what pressure would the gas be 50 per cent dissociated and what would the vapour density be at this pressure? Theoretical density of $N_2O_4 = 3.181$ (air = 1).

4. The constant, K_p, for the synthesis of NH_3 is $\log p_{NH_3}/\sqrt{p_{N_2} p_{H_2}}$ $= 2215/T - 3.626 \log T + 3.07 \times 10^{-4}T + 2.9 \times 10^{-7}T^2 + 4.82$. Calculate K_p and K_c at 1000° K.

5. For the reaction $N_2 + O_2 = 2NO$, $K = [NO]^2/[N_2][O_2]$ is given by $\log \sqrt{K} = \log 0.0249 - 2.148(2200 - T)/T$. Calculate the degree of dissociation at 2500° K.

6. In the reduction: $2AgI + H_2 \rightleftharpoons 2Ag + 2HI$, the composition of the gas coming from the reaction vessel is such that at 700° C. $p_{HI}/p_{H_2} = 1.04 \times 10^{-2}$ (extrapolated to zero gas velocity). If $\log K = \log p_{H_2} p_{I_2}/p^2_{HI} = -540.4/T + 0.503 \log T - 2.35$, calculate the partial pressure of I_2 in the vapour, the total pressure being 1 atm. (Hint: The partial pressure of I_2 is very small; $p_{H_2} + p_{HI} = 1$.]

7. In the reduction: $2NiI_2 + H_2 = 2Ni + 2HI$, the composition of the gas coming from the reaction vessel (extrapolated to zero velocity) is such that $p_{HI}/p_{H_2} = 11.0$ at 710° C. Assuming data given in the previous exercise, calculate the partial pressure of I_2 in the vapour if the total pressure is 1 atm. (N.B. The I_2 pressure is high and cannot be neglected as in the previous example.]

8. For the reaction $2NH_3 = N_2 + 3H_2$, $\log p_{N_2} p^3_{H_2}/p^2_{NH_3} = -4111/T + 5.93 \log T - 0.00015 T - 0.37 \times 10^{-6} T^2 - 6.7$. Calculate the partial pressure of NH_3 in a mixture of 1 vol. of N_2 and 3 vols. of H_2 at 500° C. and under a pressure of 200 atm.

9. Show that the maximum yield of NO is obtained from N_2 and O_2 when the latter are present in equal vols.

10. The equilibrium constant of the water-gas equilibrium, $H_2 + CO_2 = CO + H_2O$, is given by $R \ln K_p = -10,100/T + 1.81 \ln T - 0.00445 T + 0.0_668 T^2 + 0.272 R$, where R is to be expressed in cal./1°. A mixture of 10·1 per cent CO_2 and 89·9 per cent H_2 by vol. is heated at 986° C. Calculate the percentage composition of the equilibrium mixture.

11. The equilibrium constant of the reaction C (amorph.) $+ 2H_2 =$

CH_4 is given by $\log K_p = 4583/T - 1.75 \log T + 0.0_363 T - 0.7$. Calculate the amount of H_2 (percentage) in the equilibrium mixture at 1000° C. and 1 atm.

12. The thermal decomposition of $MgSO_4$: $MgSO_4 \rightleftharpoons MgO + SO_3$; $2SO_3 = 2SO_2 + O_2$, causes a pressure of 345 mm. to be set up at 1110° C. Assuming $\log [SO_2]^2[O_2]/[SO_3]^2 = -10,373/T - 2.222 \log T + 14.585$, calculate the partial pressure of SO_2 in the equilibrium gas.

13. The thermal decomposition of Ag_2SO_4 proceeds according to the equation $2Ag_2SO_4 = 4Ag + 2SO_3 + O_2$. Assuming data in the previous exercise, calculate the partial pressure of SO_2 over Ag_2SO^4 at 1100° C. if the total pressure set up is 708.4 mm.

14. Show that the degree of dissociation of CO_2 ($CO_2 = CO + \frac{1}{2}O_2$) varies inversely as the cube root of the total pressure when p is large. If $\log [CO_2]^2/[CO]^2[O_2] = 29,589/T - 2.211 \log T + 0.001289 T + 0.0_61665 T^2 + 0.0_{11}798 T^3 - 1.8153$, calculate the degree of dissociation of CO_2 at 1400° K.

15. The dissociation pressure of NH_4I at 444° C. is 1870 mm., the vapour consisting entirely of NH_3 and HI. If the vapour is kept at this temperature the pressure rises to p, owing to the reaction $2HI = H_2 + I_2$. If $K = [H_2][I_2]/[HI]^2 = 0.0198$, calculate p.

16. The value of the equilibrium constant $K_c = [HCl]^2/[H_2][Cl_2]$ at 900° abs. is $10^{11.40}$, and the fractional dissociation of water vapour at the same temperature and at 1 atm. pressure is $10^{-7.49}$. Calculate for this temperature the Deacon reaction constant $K_p = p^2_{H_2O} p^2_{Cl_2}/p_{O_2} p^4_{HCl}$, pressure being expressed in atm. (Lond. B.Sc. Special, 1926.)

17. Se dissociates according to the equation $Se_6 \rightleftharpoons 3Se_2$; 0.0755 g. of Se at 700° C. and 185 mm. pressure was found to occupy a vol. of 114.2 c.c. Calculate the degree of dissociation and the equilibrium constant, K_p. (Manc. Hons. Chem., 1926.)

(2) Reaction Isotherm.

The free energy change or *affinity* of the reaction $n_1 G_1 + n_2 G_2 + \ldots = n_1' G_1' + n_2' G_2' + \ldots$ is given by

$$A = -\Delta F$$
$$= RT \ln K - RT \ln(C_1'^{n_1'} \times C_2'^{n_2'} \times \ldots / C_1^{n_1} \times C_2^{n_2} \times \ldots)$$
$$+ (n_1' + n_2' + \ldots - n_1 - n_2 - \ldots)RT, \qquad . \quad (132)$$

or, more briefly,

$$A = -\Delta F = RT \ln K - RT \Sigma n_1 \ln C_1 + RT \Sigma n_1. \quad (132)$$

In these equations A represents the maximum work obtainable by the isothermal, reversible transformation of n_1 mols of G_1 at concentration C_1, n_2 mols of G_2 at concentration C_2, ... into n_1' mols of G_1' at concentration C_1', n_2' mols of G_2' at con-

centration $C_2' \ldots$, the temperature being T. To distinguish the *free concentrations* C from the *equilibrium concentrations* c used in forming K, they are written in Roman capitals.

The final term in (132) represents external work, which is not always recovered. If it is neglected, the equation becomes (cf. p. 34):

$$A' = -\Delta Z = RT \ln K - RT \Sigma n_1 \ln C_1. \quad (133)$$

If the free concentrations (more strictly, the *activities*) are unity, then each substance is in its standard state and A' then represents the *standard affinity*:

$$A' = RT \ln K = 4 \cdot 576\ T \log K \text{ cal.} \quad . \quad (134)$$

If the reaction proceeds without vol. change, $A = A'$.

Analogous equations in terms of partial pressures may be deduced:

$$A = RT \ln K' - RT \Sigma n_1 \ln p_1 + RT \Sigma n_1, \quad (132a)$$

$$A' = RT \ln K' - RT \Sigma n_1 \ln p_1. \quad . \quad . \quad (133a)$$

When the initial and final substances are under the same free pressure, p, then

$$A' = RT \ln K' = 4 \cdot 576\ T \log K' \text{ cal.} \quad . \quad (134a)$$

Units.—The numerical value of A depends entirely on the units of RT. It is independent of the pressure units of K_p and is the same whether K_p or K_c is used.

(3) Reaction Isochore.

The variation of K with T is expressed by the *reaction isochore*:

$$d \ln K / dT = Q / RT^2, \quad . \quad . \quad (135)$$

or $$\log K_2 / K_1 = (Q / 2 \cdot 3R)(1/T_1 - 1/T_2), \quad (135a)$$

where Q is Q_v or Q_p according as K is K_c or K_p. The integration of (135) gives (135a) on the assumption that Q is independent of T, which, is nearly true when $T_1 - T_2$ is small. The variation of Q with T is given by (54a); if the specific heats of each of the substances can be represented by a function of the form $c = a + bT + dT^2 + \ldots$, then $Q = Q_0 +$

$(\Sigma a)T + \frac{1}{2}(\Sigma b)T^2 + \frac{1}{3}(\Sigma d)T^3 + \ldots$ If this is substituted in (135), one obtains:

$$\ln K = - Q_0/RT + (\Sigma a/R)\ln T + (\Sigma b)T/2R$$
$$+ (\Sigma d)T^2/6R + \ldots + I, \qquad (136)$$

where I is an integration constant which may be calculated when K is known for one temperature. This may be obtained at 25° from affinity tables (p. 38). Owing to the experimental difficulties in measuring K, the value of I obtained from one value of K may be erroneous. Let $\mathcal{J} = - R \ln K + (\Sigma a) \ln T + (\Sigma b)T/2 + (\Sigma d)T^2/6 + \ldots$. Then, from (136), $\mathcal{J} = Q_0/T - I$ and the plot of $\mathcal{J}$ against $1/T$ gives a straight line of slope Q_0. The mean value of I is obtained by calculating the difference between the computed values of Q_0/T and $\mathcal{J}$ for each point on the line and finding the mean.

If K is given for a series of values of T and it is desired to find Q at some given temperature, equation (135) may be used graphically: $d(R \ln K)/d(1/T) = - \bar{Q} = Q$. The slope of the graph of R lnK against $1/T$ at any point is equal to $\bar{Q}$ for that point.

EXAMPLES.—1. The percentage of NO formed by passing air (79·2 vol. per cent N_2 and 20·8 vol. per cent O_2) over Pt at 1873° K. is 0·79 by vol. The heat of the reaction $N_2 + O_2 = 2NO$ is $-43,200$ cal. Calculate the percentage dissociation of NO at 3500° K.

Let P be the total pressure at 1873° K. The reaction is $N_2 + O_2 = 2NO$ and $K' = p^2_{NO}/p_{N_2}p_{O_2}$; also $p_{NO} = 0.0079\,P$, $p_{O_2} = (0.208 - \frac{1}{2} \times 0.0079)P = 0.204\,P$, and $p_{N_2} = (0.792 - \frac{1}{2} \times 0.0079)P = 0.788\,P$. Hence, $K' = (0.0079)^2 P^2/0.204 \times 0.788\,P^2 = 0.000388$. To find K' at 3500° K. use (134): $\log K' = (Q/4.576\,T) + c$ or $- 3.4110 = -43,200/4.576 \times 1873 + c$, whence $c = 1.634$. Hence $\log K' = -9446/T + 1.634$, and when T = 3500° K., $\log K' = \bar{2}.935$ or $K' = 0.0861$, so that K' (the " K " for the reaction $2NO = N_2 + O_2$) $= 1/0.0861 = 11.6$ at 3500° K. Since no vol. change occurs in the reaction, $K' = K$, and if x is the required degree of dissociation, $x^2/(1 - x)^2 = K = 11.6$, whence $x = 0.77$ or 77 per cent.

2. The mol. heats of C (graphite), CO_2, and CO at constant pressure are: C, $1.10 + 0.0048\,T - 0.0_512\,T^2$; CO_2, $7.0 + 0.0071\,T - 0.0_5186\,T^2$; CO, $6.5 + 0.0010\,T$. The heat of formation of CO_2 from graphite is 94,250 cal./mol at 18° and the heat of combustion of CO is 68,100 cal./mol at the same temperature. Calculate the heat of formation of CO from C at 1000° C.

If CO_2 is passed over C at this temperature the issuing gas contains 99·4 per cent of CO. Show that ΔZ for the reaction is 29,220 cal. at 25° C.

Applying (54) in the manner shown on p. 29 we have $Q = -40,923 - 4\cdot9\,T + 0\cdot005\,T^2 - 0\cdot0_5102\,T^3$ for the reaction $C + CO_2 = 2CO$. For $T = 1273$, $Q = -41,163$, i.e. *41,163 cals.* are *absorbed* at $1000°$ C. per 2CO.

For the reaction $C + CO_2 = 2CO$, $K_p = p^2_{CO}/p_{CO_2} = (0\cdot994)^2/0\cdot006 = 164\cdot7$ at $1000°$ C. From this we have to find K_p at $25°$. Rewriting the equation for Q: $Q = 40,923 + 4\cdot9\,T - 0\cdot005\,T^2 + 0\cdot0_5102\,T^3$, we have, using (135; cf. 136), $\ln K = -40,923/RT + 4\cdot9\,\ln T/R - 0\cdot005\,T/R + 0\cdot0_651\,T^2/R + I$, where I is some constant. When $T = 1273$, $K = 164\cdot7$; hence $I = -12\cdot84$ and $\Delta Z = -RT\ln K = 40,923 - 4\cdot9\,T\ln T + 0\cdot005\,T^2 - 0\cdot0_651\,T^3 - 12\cdot84\,T$, whence at $T = 298°$ K., $\Delta Z = 29,220\ cal.$

3. Calculate the affinity of O_2 for Fe in the atmosphere to form FeO at $1000°$ K., if the dissociation pressure of this oxide at this temperature is $3\cdot1 \times 10^{-18}$ mm.

The equilibrium constant of the reaction $2Fe + O_2 = 2FeO$ is $K' = 760/3\cdot1 \times 10^{-18}$ and the partial pressure of O_2 in the atmosphere is $0\cdot2$ atm. Hence $A' = RT\ln K' - RT\ln p = 4\cdot576 \times 1000$ $(\log 760/3\cdot1 \times 10^{-18} - \log 1/0\cdot2) = 90,000\ cals.$ per 2 mols of FeO.

4. According to Haber, $K = [CO_2][H_2]/[H_2O][CO]$ for the reaction $H_2O + CO = CO_2 + H_2$ is given by $\log K = -2116/T + 0\cdot783\,\log T - 0\cdot0_343\,T$. The heat of the reaction $CO + \frac{1}{2}O_2 = CO_2$ is 68,000 cal. (evolved) at $18°$ C. Find: (i) the heat of the reaction $H_2O + CO = CO_2 + H_2$ at $18°$; (ii) the composition of water gas formed at equilibrium at $1000°$ K.; (iii) the temperature at which the product contains 10 per cent of CO; and (iv) the heat of combustion of H_2.

$\ln K = -2\cdot3 \times 2116/T + 0\cdot783\,\ln T - 0\cdot0_343 \times 2\cdot3\,T$, and, from (135), $Q = 9672 + 1\cdot451T - 0\cdot001965\,T^2$. Hence (i) $Q = 9928\ cal.$ (absorbed) at $18°$. Subtracting the thermochemical equations $H_2O + CO = CO_2 + H_2 - 9928$ and $CO + \frac{1}{2}O_2 = CO_2 + 68,000$ we have $H_2 + \frac{1}{2}O_2 = H_2O + 77,928$, so that (iv) the heat of combustion of H_2 is $77,928\ cal.\ per\ mol.$ (evolved). The concentrations of H_2 and CO_2 and of H_2O and CO are always equal. Hence $K = [CO_2]^2/[H_2O]^2$, and at $1000°$ K. $\log K^{\frac{1}{2}} = \bar{1}\cdot9015$, so that $[CO_2]/[H_2O] = 0\cdot797$. If x mols of CO_2 are derived from 1 mol of CO, there are $1 - x$ mols of the latter left and $[CO] = [H_2O] = 1 - x$; $\therefore [CO_2]/[H_2O] = x/(1 - x) = 0\cdot797$ or $x = 0\cdot444$. The reaction mixture at $1000°$ K. contains, therefore, (ii) *27·8 per cent* each of CO and H_2O and *22·2 per cent* each of H_2 and CO_2. To answer part (iii) it must be remembered that if the reaction mixture contains 10 per cent of CO, it also contains 10 per cent of H_2O and 40 per cent each of CO_2 and H_2. Hence $K = [CO_2]^2/[H_2O]^2 = (80/20)^2 = 16$, and $\log 16 = 1\cdot2041 = -2116/T + 0\cdot783\,\log T - 0\cdot0_343\,T$, whence $T = 676°\ K.$

<p style="text-align:center">EXERCISES.—XXI</p>

1. For the reaction $N_2 + O_2 = 2NO$, $\log \sqrt{K} = 0\cdot5441 - 4725\cdot5/T$. Show that the heat of reaction is independent of T. What is its value?

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2. The equilibrium constant of the reaction $4CuO$ (s) $\rightleftharpoons$ $2Cu_2O$ (s) $+ O_2$ (g) is given by $\log K = \log p_{O_2} = -13{,}261/T + 12\cdot4$. Calculate the enthalpy change attending the formation of 1 mol of CuO from Cu_2O and O_2 at $1000°$ C.

3. The degree of dissociation of H_2S at $1100°$ K. is $0\cdot0908$ and at $1220°$ K., $0\cdot164$. Calculate the mean heat of dissociation at constant pressure.

4. Given the following equilibrium constants ($= p_{SO_3}/p_{SO_2} p_{O_2}{}^{\frac{1}{2}}$), calculate the heat of the reaction $2SO_3 \rightleftharpoons 2SO_2 + O_2$ at $750°$ C.

T (°C.) ..	528	579	627	680	727	789	832	897
K′ ..	31·3	13·8	5·54	3·24	1·86	0·956	0·627	0·358

5. Calculate the heat of the dissociation $N_2O_4 = 2NO_2$, given that the vapour density of N_2O_4 is $2\cdot65$ at $26\cdot7°$ and $1\cdot65$ at $111\cdot3°$, the theoretical vapour density for N_2O_4 being $3\cdot179$ (air = 1).

6. The equilibrium constant of the reaction $\frac{3}{2}H_2 + \frac{1}{2}N_2 = NH_3$ is given by $\log K_p = 2068/T - 2\cdot9278 \log T + 0\cdot0002756\,T + 0\cdot0_7513\,T^2 + 3\cdot149$. Calculate the heat of the reaction at $1000°$ K. What is the percentage dissociation of NH_3 at this temperature?

7. Steam at $2257°$ K. and 1 atm. is dissociated $1\cdot79$ per cent. Calculate the degree of dissociation at $1700°$ K. given that $2H_2 + O_2 = 2H_2O + 2 \times 60{,}000$ cal. at $2000°$ K.

8. The value of $[SO_2]^2[O_2]/[SO_3]^2$ at $627°$ C. is $0\cdot0_3316$; at $727°$ C., $0\cdot0_2354$, and at $832°$ C., $0\cdot0280$. Find Q_p for the intervals $627°$ to $727°$ and $727°$ to $832°$. What fraction of SO_3 is dissociated at $1000°$ C. at 1 atm.?

9. ΔZ for the reaction $CO + \frac{1}{2}O_2 = CO_2$ is given by $-67{,}510 + 2\cdot75\,T \ln T - 0\cdot0028\,T^2 + 0\cdot0_631\,T^3 + 4\cdot30\,T$. What is the degree of dissociation of CO_2 at $1478°$ K.?

10. For the reaction H_2O (g) $+ \frac{1}{2}O_2 = H_2O_2$ (g), $\Delta Z = 26{,}310 + 4\cdot56\,T \ln T - 0\cdot0028\,T^2 + 0\cdot0_637\,T^3 - 11\cdot80\,T$. What pressure of H_2O_2 is in equilibrium with water vapour and O_2 at $2000°$ K.?

11. $0\cdot02225$ g. of oxalic acid was completely decomposed at $434\cdot5°$ in a vessel of volume $20\cdot40$ c.c. at this temperature connected to a Hg manometer: $(COOH)_2 = H\cdot COOH + CO_2$; $(H\cdot COOH)_2 \rightleftharpoons 2H\cdot COOH$. The heat of dissociation of $(H\cdot COOH)_2$ is $14{,}500$ cal./mol, approximately independent of temperature, and the mass action constant $p^2_{H\cdot COOH}/p_{(H\cdot COOH)_2}$ is $0\cdot404$ at $101°$. If the vapour pressure of Hg is given by $\log p$ (mm.) $= 9\cdot9073 - (3276\cdot6/T) - 0\cdot6520 \log T$, calculate the total pressure in the vessel at equilibrium.

12. The degree of dissociation of CO_2 is $0\cdot003$ per cent at $1000°$ C. Calculate the affinity, A′, of the reaction $2CO + O_2 = 2CO_2$, each reactant being at unit pressure before and after the reaction.

13. At $1000°$ K. the degree of dissociation of steam is $3\cdot00 \times 10^{-5}$ per cent. Calculate the [standard] affinity of H_2 for O_2 at this temperature. (Manc. Hons. Chem., 1921.)

14. At $360°$ C. HI is dissociated to the extent of 20 per cent. Calculate the maximum amount of work obtainable at this temperature when 2 g. of H_2 and 254 g. of gaseous I_2 yield 256 g. of HI, both of

the reactants being initially at unit concentration and the products being finally at unit concentration. (Manc. Hons. Chem., 1920.)

15. Calculate the standard affinity of the reaction $2Ag + \frac{1}{2}O_2 = Ag_2O$ if the dissociation pressure of Ag_2O at $25°$ is 5×10^{-14} atm.

16. Calculate the affinity of Sn for the O_2 in the atmosphere to form SnO at $25°$ if the dissociation pressure of this oxide is $6\cdot771 \times 10^{-14}$ mm.. Calculate the analogous quantity for SnO_2, the dissociation pressure of which is $2\cdot107 \times 10^{-13}$ mm. at $25°$.

17. Given the following affinities, calculate the equilibrium constant of the reaction $CH_4 + H_2O = CO + 3H_2$ at $1000°$ K.: $C + CO_2 = 2CO$, $A = -37,936 + 3\cdot5406\,T\ln T - 0\cdot003136\,T^2 - RT \ln p_{CO}{}^2/p_{CO_2} + 15\cdot84\,T$; $C + 2H_2 = CH_4$, $A = 18,507 - 5\cdot9934\,T\ln T + 0\cdot002936\,T^2 - RT \ln p_{CH_4}/p_{H_2}{}^2 + 21\cdot1\,T$; $CO_2 + H_2 = CO + H_2O$, $A = -9650 + 1\cdot55\,T\ln T - 0\cdot00195\,T^2 - RT \ln p_{CO}\,p_{H_2O}/p_{CO_2}\,p_{H_2}$.

18. The heat absorbed in the formation of HI from solid I_2 at room temperature is 6150 cal./mol and the heat of sublimation of I_2 is 7550 cal./g. atom at this temperature. Given the following specific heats, C_p: HI, $6\cdot50 + 0\cdot001T$; I_2, $7\cdot4 + 0\cdot001\,T$; H_2, $6\cdot50 + 0\cdot0009\,T$, find an expression for ΔZ for the reaction $\frac{1}{2}H_2 + \frac{1}{2}I_2\,(g) = $ HI as a function of T if ln K for this reaction is $1\cdot8219$ at $793°$ K.

19. The heat of the reaction $C + O_2 = CO_2$ is $97,000$ cal. (evolved) at $291°$ K., and that of the reaction $C + \frac{1}{2}O_2 = CO$, $29,000$ cal. From the following mol. heats, C_p: CO_2, $7\cdot26 + 0\cdot0026\,T$; CO, $6\cdot45 + 0\cdot0006\,T$; C, $2\cdot10 + 0\cdot0017\,T$, and given that at $850°$ C. and 1 atm. the equilibrium gases contain $93\cdot1$ per cent of CO by vol., find an expression for the equilibrium constant of the reaction $2CO = CO_2 + C$.

20. The equilibrium constant of the reaction C (graphite) $+ 2H_2 = CH_4$ is $0\cdot00146$ at $1573°$ K. Deduce an expression for the standard affinity of this reaction and compute the value at $25°$. Mol. heats, C_p: graphite, $1\cdot1 + 0\cdot0048\,T - 0\cdot0000012\,T^2$; H_2, $6\cdot5 + 0\cdot0009\,T$; CH_4, $7\cdot5 + 0\cdot005\,T$. At room temperature the heat of combustion of CH_4 to CO_2 and H_2O is $212,400$ cal.; the heat of formation of liquid water is $68,330$ cal. and the heat of combustion of graphite is $94,250$ cal.

(b) Velocity of Reaction

(1) General.

The fundamental law is that the rate at which a substance disappears from a homogeneous system undergoing chemical change is proportional to its active mass, which is usually identified with its concentration raised to the power of the number of molecules of the substance taking part in the reaction. If the reverse reaction occurs at the same time a state of equilibrium may be set up, when the velocities of the forward and back reactions become equal; if the velocity constant of the forward reaction is very large compared with

that of the back reaction, the change proceeds practically to completion.

Consider the reaction:

$$n_1 A_1 + n_2 A_2 + n_3 A_3 + \ldots = n_1' A_1' + n_2' A_2' \cdot$$
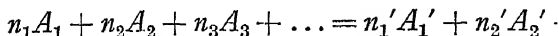
Velocity $= V = v - v'$

$$= k\, c_1{}^{n_1} c_2{}^{n_2} c_3{}^{n_3} \ldots - k'\, c_1'{}^{n_1'} c_2'{}^{n_2'} c_3'{}^{n_3'} \ldots . \quad (137)$$

For *equilibrium*

$$V = 0; \quad \therefore \quad k\, c_1{}^{n_1} c_2{}^{n_2} c_3{}^{n_3} \ldots = k'\, c_1'{}^{n_1'} c_2'{}^{n_2'} c_3'{}^{n_3'} \ldots$$

or $\quad c_1'{}^{n_1'} c_2'{}^{n_2'} c_3'{}^{n_3'} \ldots / c_1{}^{n_1} c_2{}^{n_2} c_3{}^{n_3} \ldots = k/k' = \mathrm{K}, \quad (138)$

where K is the *equilibrium constant*, which is equal to the ratio of the *velocity constants* k and k'.

When a single uncomplicated change takes place the reaction is said to be *isolated*; *simultaneous* reactions are those in which side reactions occur.[*]

(2) Unimolecular Reactions.

$A \rightarrow B + C + \ldots$. If a is the initial concentration of A and x is the amount converted after time t, then $- d(a - x)/dt = + dx/dt = k_1(a - x)$, where k_1 is a constant for a given temperature; and since $x = 0$ when $t = 0$ this becomes

$$k_1 = 1/t \cdot \ln a/(a - x) = 2 \cdot 3/t \cdot \log a/(a - x). \quad . \quad (139)$$

k_1 is a measure of the reaction rate since it represents the number of mols of A disappearing per *minute* (the practical unit of time) from 1 l. of solution containing 1 mol of A, the latter concentration being supposed maintained constant. If x_1 and x_2 are the amounts of A converted in times t_1, t_2, then

$$: \frac{2 \cdot 3}{t_2 - t_1} \log \frac{\iota}{.}$$

Plotting $\log(a - x)$ against t (preferably on semi-log paper) enables k_1 to be calculated when a is unknown. Equation (139) may be written $(a - x) = a e^{-kt} = a r^t$, where r is a constant ($=$ fraction of A changed in unit time). k_1 is independent of the unit of concentration.

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[*] For calculations based on the subject matter of this chapter see *H. M.* and Hitchcock and Robinson, *Differential Equations in Applied Chemistry* (New York, 1923).

(3) Bimolecular Reactions:

$A + B \to C + D + \dots$; A and B may be identical. If x mols of A and of B, the initial concentrations of which are a and b, are converted in time t, then $dx/dt = k_2(a - x)(b - x)$, where k_2 is the velocity constant, or

$$k_2 = 1/t(a - b) \cdot \ln b(a - x)/a(b - x) \quad . \quad (140)$$
$$= 2 \cdot 3/t(a - b) \cdot \log b(a - x)/a(b - x). \quad (140a)$$

If $a = b$, then

$$k_2 = 1/t \cdot x/(a - x). \quad . \quad . \quad . \quad (140b)$$

Obviously $\log (a - x)/(b - x)$ is a linear function of t. On expanding (140) we have:

$$k_2 = \frac{1}{t} \left\{ \frac{x}{ab} + \frac{a + b}{a^2b^2} \cdot \frac{x^2}{2} + \frac{a^2 + ab + b^2}{a^3b^3} \cdot \frac{x^3}{3} + \dots \right\}, \quad (140c)$$

which should be used in preference to (140) when a and b are not very different. When one substance is present in large excess, e.g. b large in comparison with a, $b - x = b$ and $k_2(a - b) = k' = 1/t \cdot \ln (a - x)/a$, which is the equation for a unimolecular reaction (cf. equation 139).

(4) Termolecular Reactions.

$A + B + C \to D + E + \dots$. If x mols of each of the reactants, the initial concentrations of which are a, b, and c respectively, are converted in time t, then $dx/dt = k_3(a - x)(b - x)(c - x)$, or

$$k_3 =$$
$$\frac{(b-c)\ln(a-x)/a + (c-a)\ln(b-x)/b + (a-b)\ln(c-x)/c}{(a-b)(b-c)(c-a)t}. \quad (141)$$

All the velocity equations are deducible* from :

$$dx/dt = k(a - lx)^l(b - mx)^m(c - nx)^n \dots, \quad (142)$$

where a, b, c, $\dots$ mols of A, B, C, $\dots$ take part in an undisturbed reaction; l, m, n, $\dots$ are the numbers of mols of A, B, C, $\dots$ which must react simultaneously before the change takes place; and x is the actual fall in concentration

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* Coutie, *J. C. S.*, 1927, p. 887.

in time t of a substance of which only *one* molecule is necessary for the progress of the reaction. If $A = B = C$,

$$dx/dt = k \cdot (a - 3x)^3. \quad \cdot \quad \cdot \quad \cdot \quad (143)$$

If two substances A, B are involved, with initial concentrations a, b, and 2 mols of B react with one of A,

$$dx/dt = k(a - x)(b - 2x)^2. \quad \cdot \quad \cdot \quad (144)$$

In (143) x is the reduction in concentration in time t due to *each* mol reacting, and if we put $x' = 3x$, $k' = 3k$ we may write:

$$dx'/dt = k'(a - x')^3, \quad \cdot \quad \cdot \quad \cdot \quad (145)$$

in which case

$$k' = [1/(a - x')^2 - 1/a^2]/2t. \quad \cdot \quad \cdot \quad (146)$$

(5) Order of Reaction.

The following methods are available for determining the order, n, of a reaction.

(i) *Direct Method.*—The experimental data are inserted in (139), (140), and (141). That equation giving reasonably constant values for k is considered to represent the order of the reaction. This is not a good method.

(ii) *Ostwald's " Isolation " Method.*—The order is artificially lowered by using each constituent, in turn, at a very low concentration, so that the concentrations of the other reactants remain practically constant. Thus in determining the equation giving a constant k the number of mols of the suppressed reactant taking part in the reaction is determined. The order of the total reaction is the sum of these orders.

(iii) *Van't Hoff's Differential Method.*—Two experiments are carried out with different initial concentrations, a_1 and a_2. Then

$$n = (\log da_1/dt - \log da_2/dt)/(\log a_1 - \log a_2). \quad (147)$$

For practical purposes $da/dt = \Delta a/\Delta t$.

(iv) *Ostwald's " Fraction " Method.*—The reaction rate is determined for two initial concentrations, a_1 and a_2. The times, t_1 and t_2, corresponding to the conversion of some given fraction of the substance are determined. Then

$$t_1/t_2 = a_2^{n-1}/a_1^{n-1}. \quad \cdot \quad \cdot \quad \cdot \quad (148)$$

This gives (with certain assumptions) Noyes' expression (*H. M.*, p. 161):

$$n = 1 + \{\log(t_1/t_2)/\log(a_2/a_1)\}. \quad . \quad . \quad (149)$$

(6) Simultaneous Reactions.

(i) *Side Reactions.*—When two or more reactions proceed simultaneously and independently the velocity equations for each are united. Thus, if a substance A is being converted to C by a unimolecular reaction and simultaneously to D by a bimolecular reaction, then $dx/dt = k_1(a - x) + k_2(a - x)(b - x)$ or

$$k_2(K + b - a) = 1/t \cdot \ln a(K + b - x)/(K + b)(a - x),$$

where $K = k_1/k_2$. When two unimolecular reactions proceed side by side equation (139) holds with k_1 replaced by $k_1' + k_1''$, the velocity constants of the two reactions. An analogous statement holds for simultaneous bimolecular reactions, &c.

(ii) *Opposing Reactions.*—The net velocity of simultaneous opposing reactions is the difference between the velocities of the two reactions. The equations for dx/dt are constructed for each reaction in the usual way; they are then subtracted in order to find an equation for the net velocity, which is then integrated (cf. Ex. 2, p. 80). In this case a state of equilibrium is set up.

(iii) *Consecutive Reactions.*—When a reaction proceeds in successive stages, *consecutive reactions* are said to occur. Velocity equations are set up for each step. One or more of these equations is integrated and the value of the integral inserted in the remaining equation, which is then solved according to the usual methods (*H. M.*, p. 244).

EXAMPLES.—1. The following results were obtained for the reaction $2C_2H_5OH$ (excess) $+ 2Br_2 = CH_3 \cdot COOC_2H_5 + 4HBr$; c is the molar concentration of Br_2 at the end of t min.:

$t =$	0	3	4	6	10	15
I. .. $c \times 10^3 =$	2·07	1·57	—	1·27	1·00	0·73
II. .. $c \times 10^3 =$	4·24	—	3·14	2·49	2·24	1·78
III. .. $c \times 10^3 =$	8·14	—	6·10	—	4·45	3·73

Calculate the order of the reaction by Noyes' method; find the times for both $\frac{1}{3}$ and $\frac{1}{2}$ of Br_2 absorption. Confirm the result by calculating the order by van't Hoff's method.

Plot the curves of c against t for each experiment and read off the following figures:

Experiment	I	II	III	I	II	III
Fraction of Br_2 used	1/3	1/3	1/3	1/2	1/2	1/2
Time (min.)	5·95	6·8	7·86	10·50	12·35	14·14

According to (149), if the figures for one-third absorption are used, we find:

I and II. $n = 1 + (\log 5·95 - \log 6·8)/(\log 0·00424 - \log 0·00207)$
$= 0·81.$

II and III. $n = 1 + (\log 6·8 - \log 7·86)/(\log 0·00814 - \log 0·00424)$
$= 0·78.$

III and I. $n = 1 + (\log 7·86 - \log 5·95)/(\log 0·00207 - \log 0·00814)$
$= 0·80.$

The mean value $= 0·80$. Proceeding similarly with the results for half conversion we find the mean value $n = 0·78$. The reaction, therefore, is probably unimolecular, but disturbing side reactions are occurring. Van't Hoff's method enables n to be calculated from quantities measured at the beginning of the reaction, i.e. before the disturbing reactions have had time to become apparent. The calculation is as follows:

II. $c_0 = 0·00424$; $\Delta c_2 = 0·00424 - 0·00314 = 0·0011$; also $\Delta t_2 = 0 - 4 = -4$. Hence $\Delta c_2/\Delta t_2 = -0·00028$.

III. $c_0 = 0·00814$; $\Delta c_3 = 0·00814 - 0·00610 = 0·00204$; also $\Delta t_3 = 0 - 4 = -4$. Hence $\Delta c_3/\Delta t_3 = -0·00051$.

$\therefore n = \log(-0·00028/-0·00051)/\log(0·00424/0·00814) = 0·92.$

The process is repeated with III and I, and with II and I, the final mean being practically unity, confirming the unimolecular nature of the main reaction.

2. Set up a velocity equation for the conversion of γ-oxybutyric acid into γ-oxybutyrolactone: $CH_2OH(CH_2)_2COOH \rightleftharpoons \overline{(CH_2)_3CO-O} + H_2O$. Check the equation from the following data, which refer to the conversion of a quantity of pure acid which required 18·23 c.c. of a standard $Ba(OH)_2$ solution for neutralization. The amount of acid converted (expressed in c.c. of baryta solution), x, in t min., is

t	36	50	65	80	100	∞
	2.70	4.08	6.07	7.14	7.98	13.29

Let the initial concentration of acid be a_1 and that of lactone a_2. If amount x of acid is converted to lactone in time t, then after this time $a_1 - x$ of acid is present and $a_2 + x$ of lactone. The velocity of transformation acid $\rightarrow$ lactone is $dx_1/dt = k_1(a_1 - x)$ and that

of lactone $\longrightarrow$ acid $dx_2/dt = k'(a_2 + x)$. Hence the net velocity is $dx/dt = k_1(a_1 - x) - k'(a_2 + x)$, which on integration yields:

$$k_1 + k' = 1/t \cdot \left\{ \log\left(\frac{k_1 a_1 - k' a_2}{k_1 + k'}\right) - \log\left(\frac{k_1 a_1 - k' a_2}{k_1 + k'} - x\right) \right\}.$$

When equilibrium is reached ($t = \infty$), $dx/dt = 0$ and $(a_2 + x)/(a_1 - x) = k_1/k' = K$, the equilibrium constant, or

$$\frac{1}{t} \log \frac{K a_1 - a_2}{K a_1 - a_2 - (K + 1)x} = k_1 + k',$$

which is the required equation.

To confirm numerically, first evaluate K. Since $a_2 = 0$, $K = 13 \cdot 29/(18 \cdot 23 - 13 \cdot 29) = 2 \cdot 69$. Then $k_1 + k' = 1/t \cdot \log 2 \cdot 69 \, a_1/(2 \cdot 69 \, a_1 - 3 \cdot 69 \, x) = 1/t \cdot \log 49 \cdot 05/(49 \cdot 05 - 3 \cdot 69 \, x)$, which may be evaluated with the values of x given. $k_1 + k'$ is approx. $0 \cdot 04$.

3. Show that the thermal decomposition of N_2O_5 ($2N_2O_5 \longrightarrow 2N_2O_4 + O_2 \rightleftharpoons 4NO_2 + O_2$) at 55° is a unimolecular gas reaction from the following observed total pressures (mm.):

p_t ..	424·5	449·0	471·5	491·8	524·8	604·0	654·5	673·7
t (min.)	3	4	5	6	8	16	30	∞

For the dissociation $2NO_2 \rightleftharpoons N_2O_4$, $\log K' = \log p_{N_2O_4}/p^2_{NO_2} = 2866/T - \log T - 9 \cdot 132$. (N.B. Owing to the inevitable commencement of the reaction before measurements can be begun the initial pressure of undecomposed N_2O_5, p_i, must be calculated.)

If the reaction is unimolecular then $k_1 t = \ln(\text{initial concentration } N_2O_5)/(\text{concentration } N_2O_5 \text{ after time } t) = \ln p_i/(p_i - p)$, or $k_1(t_2 - t_1) = 2 \cdot 303 \log(p_i - p_1)/(p_i - p_2)$. To calculate p_i note that p_{O_2} is independent of α, the degree of dissociation of N_2O_4, so that all quantities may be expressed in terms of α and p_{O_2}. In the dissociation $N_2O_4 \rightleftharpoons 2NO_2$ we have $K' = p_{N_2O_4}/p^2_{NO_2} = 2p_{O_2}(1 - \alpha)/(4\alpha p_{O_2})^2$, or $\alpha^2/(1 - \alpha) = 1/8p_{O_2}K'$, which enables α to be calculated from a knowledge of K' at any given temperature for a series of *arbitrary* p_{O_2} values. But, after complete decomposition of N_2O_5, the final pressure $= p_f = p_{N_2O_4} + p_{NO_2} + p_{O_2} = 3p_{O_2} + 2\alpha p_{O_2}$, i.e. when α is known p_f is a known function of p_{O_2}. Also, $p_i = 2p_{O_2}$ when decomposition is complete, so that by giving p_{O_2} a series of arbitrary values corresponding values of α are obtained and p_i can be plotted against p_f [$= (1 \cdot 5 + \alpha)p_i$]. In this way the value of p_i corresponding with $p_f = 673 \cdot 7$ mm. is found to be $331 \cdot 3$ mm.

The partial pressure of N_2O_5 remaining after time t is $(p_i - p)$. The total pressure is $(p_i - p) + p_{N_2O_4} + p_{NO_2} + p_{O_2} = p_t$. Hence $p_t - p_i = p_0 + 2\alpha p_{O_2} = (\alpha + 0 \cdot 5)p$. α is calculated as above; p_t is observed; p_i is known and so p is calculated. By plotting arbitrary values of $p_t - p_i$ against p, the values of p corresponding to the observed values of $p_t - p_i$ may be read off as follows:

t ..	3	4	5	6	8	16	30
p ..	72·9	95·0	115·9	135·2	168·0	252·2	309·0

From these values k_1 is calculated readily; the mean value is about 90×10^3.

Note on Gas Reactions.—The apparent order of reactions in the case of gases is often no guide as to the order of the reaction *in* the gas itself, since many such reactions take place on the surface of the containing vessel. There are very few (if any) *true* homogeneous gas reactions; the thermal decomposition of N_2O_5 is said to be one.*

EXERCISES.—XXII

1. Demonstrate the unimolecularity of the conversion of aceto-chloranilide into *p*-chloracetanilide from the following figures. Portions of the reaction mixture were withdrawn after t hr. and treated with KI, the liberated I_2 being titrated with $Na_2S_2O_3$ solution. Only acetochloranilide reacts with KI. x refers to the total reaction mixture.

t	0	1	2	3	4	6	8
x (c.c. $Na_2S_2O_3$)	49·3	35·6	25·75	18·5	13·8	7·3	4·8

2. The spontaneous change of Ra emanation is a unimolecular reaction. The results obtained were:

Time	0	7	11	14	16·5	20	25	36	45	64	75
Vol.	0·102	·062	·044	·033	·025	·019	·016	·007	·003	·002	·000

Show how these figures fit the order of the reaction. (Lond. B.Sc. Hons., 1907.)

3. The change with time of the angle of rotation of a sucrose solution at $25°$ containing $N/2$ HCl is as follows:

t (min.) ..	0	176	∞
α ..	25·16	5·46	$-8·38°$

Find an expression connecting t with the rotation and calculate the rotation of the solution after 236 min.

4. Construct an equation for the velocity constant of the catalytic hydrolysis of methyl acetate in presence of acetic acid. Assume that the inital concentration of the ester is b; that x mols of acetic acid are liberated after time t, whilst a mols of acetic acid are present at any given moment.

5. The following figures refer to the reaction $2HgCl_2 + HCOONa = Hg_2Cl_2 + KCl + HCl + CO_2$. a is the concentration of $HgCl_2$ and b that of HCOONa.

t (hr.)	0	3	0	3	0	2·2	0	1
a ..	0·1034	0·0679	0·0503	0·0326	0·1028	—	0·1028	—
b ..	0·1737	—	0·1737	—	0·3790	0·3279	1·0227	0·9579

What is the order of the reaction?

* See Hinshelwood, *Kinetics of Chemical Change in Gaseous Systems*, 1926.

6. Show that equation (140) may be written a/b (constant)$^t =$ $(a - x)/(b - x)$. A solution containing 35·35 units of $Na_2S_2O_3$ and 18·25 units of MeI contained after 10 min. 27 units and 9·9 units, respectively, and after 20 min. 23·2 units and 6·1 units. Show that the reaction is probably bimolecular.

7. The following figures refer to the rotation, α, of a solution of lactose hydrate which undergoes lactone formation in aqueous solution: $C_{12}H_{24}O_{12} \rightleftharpoons C_{12}H_{22}O_{11} + H_2O$:

t (min.)	0	15	60	120	180	240	300	∞
α ..	8·98	8·77	8·23	7·67	7·18	6·83	6·53	5·65

Show that the change is an opposing unimolecular reaction.

8. The experiment in the previous exercise was repeated in the presence of the solid hydrate:

t (min.)	0	60	120	180	300	420	∞
α ..	11·30	11·80	12·29	12·60	13·10	13·63	16·23

Using the data in Exercise 7, and given that the specific rotation of the equilibrium mixture is 52·5° and that of the hydrate 82·5°, calculate the specific rotation of the lactone.

9. The following results refer to the reaction H.COOH + EtOH $\rightleftharpoons$ H.COOEt + H_2O, carried out with EtOH and water in large excess. Construct an equation representing the reaction and check it. The solution contains HCl (catalyst): $y =$ c.c. of $N/100$ Ba(OH)$_2$ necessary to neutralize 5 c.c. of the reaction mixture.

t (min.)	0	50	100	160	290	∞
	43·52	40·40	37·75	35·10	31·09	24·29

10. The following figures relate to the hydrolysis of Me acetate in dilute MeCOOH solution. y represents the amount of free acid at the end of t min. expressed in arbitrary units; the initial concentration of acetic acid is 1338 units and that of methyl acetate 1370 units. Construct a velocity equation for the reaction and check it.

t ..	7200	14,400	21,600	28,800	34,500
y ..	1565	1747	1912	2057	2153

[Hint.—The velocity of hydrolysis at a given instant is proportional to the concentration of the catalyst at that instant.]

11. Find the apparent order of the reaction $2CO = CO_2 + C$ at 310° if in one experiment the CO pressure dropped from 786·8 mm. of Hg to 693 mm. in 30 min. and in a second experiment from 535·3 mm. to 468·1 mm. in the same time.

(c) DISTRIBUTION LAW

(1) Distribution (or Partition) Law.

The ratio of the concentrations of a molecular species distributed between two phases in equilibrium is constant at constant temperature:

$$c_1/c_2 = k. \quad \ldots \ldots \quad (150)$$

k is the *distribution* or *partition coefficient*.

(2) Application to Gas-liquid Systems—Law of Henry and Dalton.

The mass of gas, m, dissolved by a given volume of liquid is, at a given temperature, proportional to the pressure (or partial pressure), p, when equilibrium is reached:

$$m/p = \text{constant}. \quad \ldots \ldots \quad (151)$$

Compound formation in solution does not invalidate the law, but only changes the value of the constant.

Equation (150) gives

$$\frac{\text{concentration of gas in liquid phase}}{\text{concentration of gas in vapour phase}} = s \quad (152)$$

where s is the *solubility* or *Ostwald solubility coefficient* of the gas. It is the vol. of gas, measured at $t°$ and p atm., dissolved by unit volume of liquid when the gas pressure in equilibrium is p atm. *Bunsen's absorption coefficient*, β, is the vol. of gas, reduced to S.T.P., absorbed by unit vol. of liquid at 1 atm. pressure: $s/\beta = T/273$.

EXAMPLES.—1. The solubility coefficient of O_2 in water is 0·04 at 0°. Calculate the weight of O_2 which will dissolve in 10 l. of water at 0° under a pressure of 40 atm.

Concentration at 1 atm. $= 1/22\cdot4$ mol /l., and concentration under 40 atm. $= 40/22\cdot4$ mol/l. Hence, for 1 l. of water, from (152): concentration in liquid phase$/(40/22\cdot4) = 0\cdot04$, so that concentration of gas in water $= 0\cdot04 \times 40/22\cdot4$ mol/l., and weight of gas dissolved in 10 l. $= 10 \times 32 \times 0\cdot04 \times 40/22\cdot4 = 22\cdot9$ *g*., nearly.

2. 16 c.c. of dry gas at 15° are confined over Hg in a barometer tube, the Hg standing at 232 mm. whilst the barometric pressure is 755 mm. 2 c.c. of water are introduced into the tube. The vol. of gas becomes 14·5 c.c., and the height of the Hg in the tube 235 mm.

Calculate the absorption coefficient and the Ostwald solubility co-efficient of the gas.

Vol. of dry gas at S.T.P. before absorption $= 16 \times (755 - 232) \times 273/760 \times 288 = 10\cdot44$ c.c. The vapour pressure of water at $15° = 12\cdot8$ mm.; $\therefore$ pressure of dry gas after absorption $= 755 - 235 - 12\cdot8 = 507\cdot2$ mm., and its vol. at S.T.P. $= 14\cdot5 \times 507\cdot2 \times 273/760 \times 288 = 9\cdot175$ c.c. Hence, vol. at S.T.P. of gas, absorbed by 2 c.c. of water at $15° = 10\cdot44 - 9\cdot175 = 1\cdot265$ c.c. Absorption coefficient $=$ vol. dissolved by 1 c.c. of water at 760 mm. $= 1\cdot265 \times 760/507\cdot2 \times 2 = 0\cdot9475$.

The solubility coefficient, s, is $\beta(273 + t)/273 = 0\cdot9475(288)/273 = 0\cdot9997$.

3. A *closed* vessel of 2 l. capacity contains initially 1 l. of water and 1 l. of air at 0° and 1 atm. The absorption coefficients at 0° are: O_2, $0\cdot04980$; N_2, $0\cdot02388$; A, $0\cdot05780$. The composition of air in percentages by vol. is: N_2, $78\cdot06$; O_2, $21\cdot00$; A, $0\cdot94$. The partial pressure of water at 0° is $4\cdot58$ mm. Find the partial pressures and the total pressure when the liquid is saturated. Find, also, the per-centage vol. composition of the (dry) gas obtained on boiling the solution.

The solubility and absorption coefficients are identical at 0°. The solution takes place in a closed vessel; let p atm. be the equilibrium pressure of the O_2. Total pressure of air $= 760 - 4\cdot58 = 755\cdot42$ mm., and initial partial pressure of $O_2 = 21 \times 755\cdot42/100 = 158\cdot6$ mm. Now 1 mol of O_2 occupies $22\cdot4$ l. at 760 mm. and 0°; hence $1 \times 158\cdot6/760 \times 22\cdot4 = 0\cdot00932$ mol occupies 1 l. at $158\cdot6$ mm. $=$ initial concentration of O_2. Concentration of O_2 at equilibrium $= p/22\cdot4$ mol/l. Hence, from (152), concentration of gas in liquid $= 0\cdot04980p/22\cdot4 = 0\cdot002223p$ mol/l. The number of mols of O_2 left $= 0\cdot00932 - 0\cdot002223p$. Equation (72) gives: $p \times 1 = (0\cdot00932 - 0\cdot002223p) \times 0\cdot082 \times 273$ or $p = 0\cdot199$ atm. or 151 mm. $=$ partial pressure of O_2. We find similarly: initial partial pressure of $N_2 = 78\cdot06 \times 755\cdot42/100 = 589\cdot5$ mm. initial number of mols of $N_2 = 589\cdot5/760 \times 22\cdot4 = 0\cdot03463$; concentration of N_2 in liquid (mols/l.) $= 0\cdot02388p'/22\cdot4 = 0\cdot001066p'$; number of mols left in gas $= 0\cdot03463 - 0\cdot001066p'$ $\therefore$ $p' =$ partial pressure of $N_2 = 575\cdot6$ mm.; also $p'' =$ partial pressure of A is found to be $6\cdot71$ mm. Total pressure when liquid is saturated $= 151 + 575\cdot6 + 6\cdot71 = 733\cdot31$ mm. $= 0\cdot965$ atm.

The composition of the gas expelled by boiling will be $0\cdot002223p$ mol O_2, $0\cdot001066p'$ mol N_2, and $0\cdot00258p''$ mol A, i.e. $0\cdot0004424$ O_2; $0\cdot0008069$ N_2, and $0\cdot00002278$ A. Total number of mols $= 0\cdot001272$ $\therefore$ *percentage* $O_2 = 34\cdot8$, *percentage* $N_2 = 63\cdot4$, *percentage* $A = 1\cdot8$.

4. Calculate the mol. hydration of sucrose (M $= 342$) in a $16\cdot67$ per cent so ution if 1 l. of the solution at 15° absorbs $15\cdot61$ c.c. of H_2, given that 1 l. of water dissolves $18\cdot83$ c.c. of H_2 at the same temperature. The density of the sugar solution is $1\cdot0705$.

In a $16\cdot67$ per cent sucrose solution there are $83\cdot33$ g. of water per 100 g. of solution, so that 1 l. of solution contains $833\cdot3 \times 1\cdot0705 = 892$ g. of water. Hence $15\cdot61$ c.c. of H_2 are absorbed by 892 g.

of water in solution, or 17·5 c.c. of H_2 is absorbed by 1 1. of water in solution. If this water were all " free " it would have absorbed 18·83 c.c. of H_2, so that the fraction $(18·83 - 17·5)/18·83 = 1·33/$ 18·83 of the water is attached to the solute. Hence the average number of water molecules per mol of sucrose $= 1·33 \times 83·33 \times 342/18·83 \times 16·67 \times 18 = 6·7$. [The value 5·3 is obtained from osmotic pressure results: A. W. Porter, 1917.]

5. Determine the hydrolysis constant, K_h, of NaClO from the following data. A $0·3663 \times 10^{-3}M$ solution of HClO on distillation yielded 15·1 c.c. of distillate equivalent to 14·84 c.c. of $N/500$ $Na_2S_2O_3$. A $7·135 \times 10^{-3}M$ solution of NaClO on distillation yielded 15·00 c.c. of distillate equivalent to 3·37 c.c. of $N/500$ $Na_2S_2O_3$. (It is assumed that the distillate is very small in bulk compared with the solution being distilled. $2KI + HClO = KCl + I_2 + KOH$; the latter is removed by addition of acid.)

In the first experiment (concentration of distillate)/(concentration of HClO in solution) $= (14·84 \times 10^{-3}M/15·1)/(0·3663 \times 10^{-3} \times M)$ $= 2·683$; since the distillate is very small in bulk compared with the main solution, this represents the partition coefficient of HClO between the vapour phase and the solution, which is constant. Hence in the distillation of the NaClO solution, if $c' =$ [HClO] in this solution, $2·683 =$ concentration of distillate$/c' = (3·37 \times 10^{-3}M/15·00)/c'M$; or $c' = 0·08373 \times 10^{-3}$. If $x =$ degree of hydrolysis and $c =$ concentration of NaClO solution:

$$NaClO + H_2O = NaOH + HClO,$$
$$(1 - x)c \qquad\qquad xc \qquad xc$$
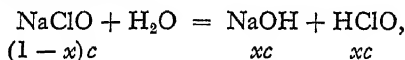
so that $K_h = x^2c^2/(c - xc)$. Since $c = 7·135 \times 10^{-3}$, and $xc = c' = 0·08373 \times 10^{-3}$, $K_h = 0·995 \times 10^{-6}$.

EXERCISES.—XXIII

1. The concentrations of Cl_2 gas, c_1 (millimol/l.), over a CCl_4 solution of concentration c_2 are as follows at 0° C.:

c_1	..	0·1109	0·2666	0·5365	0·8800
c_2	..	8·908	22·46	44·14	75·09

What can be concluded as to the state of Cl_2 in CCl_4 solution?

2. The vols. of O_2 in c.c. (reduced to S.T.P.) absorbed by 10·87 g. of Ag at 1075° under a pressure of p mm. are:

p	..	1203	760	488	346	39
v	..	26·91	21·01	17·02	14·53	4·75

The O_2 may dissolve as such, may be present in the monatomic condition, or may be present as Ag_2O. Which alternative is supported by the above figures?

3. 27·22 c.c. of 98 per cent H_2SO_4 at 18·5° and 714·6 mm. absorb 0·58 c.c. of N_2 measured under similar conditions. Calculate the solubility coefficient at 18·5° and also the absorption coefficient.

4. A closed vessel of 6 l. capacity contains 2 l. of water and a mixture of 1 l. of a gas A and 3 l. of B. The temperature is 0°; the vapour pressure of water $= 4 \cdot 6$ mm. The initial pressure of the moist gases is 740 mm., and the absorption coefficients are (at 0°): A, $0 \cdot 0498$; B, $0 \cdot 0738$. Calculate the partial pressures of the gases (in mm.) when the water is saturated.

5. A mixture of equal vols. of H_2, O_2, and CO_2 at 730 mm. is shaken with 2 l. of water at 0° (vapour pressure $= 4 \cdot 58$ mm.) in a closed vessel of 5 l. capacity. Calculate the partial pressures of the gases at equilibrium. The Bunsen absorption coefficients are: H_2, $0 \cdot 02153$; O_2, $0 \cdot 04924$; CO_2, $1 \cdot 7326$.

6. If air contains 79 per cent of N_2 and 21 per cent of O_2 by vol., and the solubility coefficients of these gases at 0° are $0 \cdot 04$ and $0 \cdot 02$ respectively, find the composition of the dry gas obtained by boiling water which has been saturated with air at 0°.

7. A large bulk of $0 \cdot 4661 \times 10^{-3} N$ HClO solution was distilled, and the distillate, 14·9 c.c., after treatment with KI solution and HCl required 18·76 c.c. of $N/500$ $Na_2S_2O_3$ to decolorize the liberated I_2. A large bulk of $9 \cdot 025 \times 10^{-3} N$ NaClO solution was then distilled, yielding 14·90 c.c. of distillate equivalent to 3·82 c.c. of $N/500$ $Na_2S_2O_3$. Calculate the hydrolysis constant of NaClO.

8. A $N/4$ solution of KI has a density of 1·027 and absorbs 5·49 c.c. of O_2 per l. at 0°. The solubility coefficient of O_2 is $0 \cdot 0492$ at 0°. Show that the degree of hydration of KI at this dilution is 9.

(3) Liquid-liquid Systems.

The distribution of a solute between two immiscible liquids occurs in accordance with (150). When association or dissociation occurs the concentrations of the like molecular species must be computed with the aid of the law of mass action. If c_1, c_2 are the (analytical) concentrations of the solute in phases A and B respectively and if $\alpha =$ degree of dissociation of single mols in A and $\beta =$ degree of dissociation of double mols in B, then:

Phase A.	Phase B.	k
No molecular change	No molecular change.	c_1/c_2.
Dissociation $\quad$ ..	,, $\quad$,, $\quad$,,	$c_1(1-\alpha)/c_2$.
No molecular change	Association.	$c_1/[c_2(1-\beta)]^{\frac{1}{2}}$.
Dissociation $\quad$ ..	,,	$c_1(1-\alpha)/[c_2(1-\beta)]^{\frac{1}{2}}$.

EXAMPLES.—1. The partition coefficient of PhCOOH between water and C_6H_6 is $0 \cdot 700$ at 10°. In a certain distribution experiment the water layer contained $0 \cdot 0429$ g. of acid per 200 c.c., the degree

of dissociation being 0·169, whilst in the C_6H_6 layer the concentration was 0·1449 g. per 200 c.c. Calculate the equilibrium constant of the reaction $(PhCOOH)_2 \rightleftharpoons 2PhCOOH$, expressing concentrations in g./l.

Let m be the concentration of simple mols in the C_6H_6 layer (in g./l.). Then if $\alpha =$ degree of dissociation of acid in water layer, the concentration of simple mols in the latter is $5 \times 0·0429(1 - \alpha)$ and $0·700 = 0·2145(1 - \alpha)/m = 0·1782/m$, whence $m = 0·2546$. The required constant $= K = [PhCOOH]^2/[(PhCOOH)_2] = m^2/[(5 \times 0·1449) - m] = 0·06483/0·4699 = 0·138$.

2. A litre of aniline hydrochloride solution, containing 0·0997 mol of salt, was shaken with 59 c.c. of C_6H_6 at 25°. After the attainment of equilibrium 10 c.c. of the C_6H_6 layer were found to contain 0·0129 g. of aniline. Calculate the hydrolysis constant of the hydrochloride, the percentage hydrolysis in the given solution, and the dissociation constant of aniline as a base, if the distribution ratio of aniline between C_6H_6 and H_2O is 10·1 at 25° and K_w, the ionic product for water, is $1·2 \times 10^{-14}$.

Concentration of C_6H_6 layer $= 1·29$ g./l. $= 1·29/93$ mol/l. Hence concentration of free $PhNH_2$ in water layer $= 1·29/93 \times 10·1 = 0·001393$ mol/l. The initial concentration of $PhNH_2$ (as hydrochloride and free base) in the water layer $= 0·0997$ mol/l. The amount of free aniline extracted by 59 c.c. of $C_6H_6 = 0·059 \times 1·29/93 = 0·000818$ mol, so that the equilibrium concentration of $PhNH_2$ (as hydrochloride and free base) $= 0·0997 - 0·00082 = 0·09888$ mol/l. But the concentration of free $PhNH_2$ in the water layer is 0·001373 mol/l. Hence the concentration of hydrochloride is $0·09888 - 0·00137 = 0·09751$ mol/l. Also concentration of free HCl $= 0·0997 - 0·0975 = 0·0022$ mol/l. Hence $K_h = [acid][base]/[unhydrolysed\ salt] = 0·0022 \times 0·001373/0·09751 = 0·0_43098$. If $x =$ degree of hydrolysis and $c =$ concentration, then $K_h = x^2c/(1 - x)$ or $0·0_43098 = x^2 \times 0·0997/(1 - x)$, whence $x = 1·6\ per\ cent$ approx. Also, from (172), $K_h = K_w/K_b$ or $1·2 \times 10^{-14}/3·098 \times 10^{-5} = K_b = 3·9 \times 10^{-10}$.

3. The distribution of MeCOOH between water and $CHCl_3$ is as follows (c_1, concentration in water; c_2, concentration in $CHCl_3$):

| c_1 | .. | 0·06445 | 0·1269 | 0·1946 | 0·2515 | 0·2696 |
| c_2 | .. | 0·00174 | 0·00406 | 0·007586 | 0·01109 | 0·01222 |

60 c.c. of an aqueous solution contained, per l., 0·2 g. equivalent of tartaric acid, 0·2 g. equivalent of NaOH, and 0·199 g. equivalent of MeCOOH after shaking with an equal vol. of $CHCl_3$ (which extracts MeCOOH only). The $CHCl_3$ was found to contain 0·005632 g. equivalent of acid per l. Calculate the ratio of the amount of tartaric acid to that of acetic acid in combination with the base.

The ratio c_1/c_2 is a function of concentration, owing to association of acid in $CHCl_3$ and dissociation in water. By plotting c_1/c_2 against c_2 the value of c_1/c_2 at $c_2 = 0·005632$ is found to be 28·3, whence the concentration of free acid in the aqueous layer is $28·3 \times 0·005632 = 0·1593$ g. equivalent/l. Hence the MeCOOH present as Na acetate

is $0 \cdot 199 - 0 \cdot 1593 = 0 \cdot 0397$ g. equivalent/l. The rest of the NaOH is present as Na tartrate (since insufficient base is present for complete neutralization of the acids). Hence $0 \cdot 200 - 0 \cdot 0397 = 0 \cdot 1603$ g. equivalent/l. is the concentration of Na tartrate, and the ratio in which the tartaric and acetic acids compete for the base is $0 \cdot 1603/0 \cdot 0397$, i.e. $4 : 1$. (N.B.—It is assumed that the MeCOOH is practically non-dissociated in the water solution at the concentrations involved.)

4. The distribution of salicylic acid between water and C_6H_6 is as follows:

c_1 (mol/l.)	..	$0 \cdot 0529$	$0 \cdot 2584$	$0 \cdot 0520$	$0 \cdot 3126$
c_2 (mol/l.)	..	$0 \cdot 0782$	$0 \cdot 9427$	$0 \cdot 0800$	$1 \cdot 0330$
$t°$ (C.)	..	10	10	40	40

where c_1 is the total concentration of the acid in the aqueous layer and c_2 that in the C_6H_6 layer, in which association takes place: $2HO.C_6H_4COOH \rightleftharpoons (HO.C_6H_4COOH)_2$. The mean dissociation constant of the acid at $25°$ is $0 \cdot 001$. Calculate the mean heat of association of the acid in C_6H_6 solution.

The degree of dissociation of the acid in the water layer, x, may be calculated from $0 \cdot 001 = x^2c_1/(1 - x)$; the respective values are $0 \cdot 1283$, $0 \cdot 06033$, $0 \cdot 1297$, and $0 \cdot 05498$. If $m =$ concentration of single mols in C_6H_6, and $k =$ partition coefficient, $m = c_1(1 - x)/k$. The concentration of double mols in the C_6H_6 is $(c_2 - m)$. Hence, $K = [HO.C_6H_4.COOH]^2/[(HO.C_6H_4.COOH)_2] = m^2/(c_2 - m) = [c_1 (1 - x)]^2/k^2[c_2 - c_1(1 - x)/k]$. This contains two unknowns, K and k, which may be determined from the two sets of experimental data. It is found that $k = 0 \cdot 845$ at $10°$, and $0 \cdot 687$ at $40°$, whence $K = 0 \cdot 1514$ and $0 \cdot 3065$, respectively. Hence, heat of dissociation of the double molecules is given by $\log(0 \cdot 3065/0 \cdot 1514) = Q/4 \cdot 576(1/283 - 1/313)$ or $Q = 3103$ cal. Hence heat of association is -3103 *cal.*

5. Calculate the activity coefficients of picric acid at the concentrations given from the following figures for the distribution of this substance between C_6H_6 and water ($c = $ mol/l.):

c_1 (H_2O)	$0 \cdot 0334$	$0 \cdot 0199$	$0 \cdot 0101$	$0 \cdot 00701$	$0 \cdot 00327$	$0 \cdot 00208$
c_2 (C_6H_6)	$0 \cdot 1772$	$0 \cdot 0700$	$0 \cdot 0199$	$0 \cdot 0101$	$0 \cdot 00225$	$0 \cdot 000932$

The activity of undissociated picric acid, a_2, is proportional to c_2. Also, if $c_1 = M$, $c_2^{\frac{1}{2}}/c_1 = ka_2^{\frac{1}{2}}/M = k\gamma$, where k is some constant. At infinite dilution $\gamma = 1$ and $k\gamma = k$. The plot of c_1 against $k\gamma$ may be extrapolated to $c_1 = 0$, whence $k (= k\gamma$ at $c_1 = 0) = 15 \cdot 4$. Hence $\gamma = c_2^{\frac{1}{2}}/15 \cdot 4\,c_1$, and the values are, for the respective concentrations, $0 \cdot 82$, $0 \cdot 86$, $0 \cdot 91$, $0 \cdot 93$, $0 \cdot 94$, $0 \cdot 97$.

EXERCISES.—XXIV

1. Given that the solubilities of I_2 in water and CS_2 are respectively as 1 to 590, and that the mol. condition of the I_2 is the same in both, what will be the weight of I_2 left in 1 l. of an aqueous I_2 solution, originally saturated at $18°$ C., after having been shaken with 100 c.c.

of CS_2? Solubility of I_2 at 18° C. = 1 g. in 3616 c.c. of water. (Lond. B.Sc. General, 1926.)

2. An aqueous solution of MeCOOH was shaken with C_6H_6 at 16°; the layers gave on analysis (mol/l.):

	Water Layer.	C_6H_6 Layer.	Percentage Dissociation in Water.
(i)	0·110	0·00181	1·14
(ii)	0·0334	0·000417	20·2

Assuming MeCOOH to exist partly as double molecules in the benzene solution, find the equilibrium constant $[MeCOOH]^2/[(MeCOOH)_2]$, expressing concentrations in mol/l.

3. The dissociation constant of picric acid is 0·164. It is found that a $0·02N$ aqueous picric acid solution is in equilibrium with a $0·07N$ solution in C_6H_6. If picric acid exists in the normal state in C_6H_6 solution, calculate the partition coefficient for this acid between C_6H_6 and H_2O.

4. 0·009592 mol of HgI_2 was dissolved in 1 l. of a $0·1N$ KI solution, and the resulting liquid, containing all the Hg as HgI_2, xKI, was shaken at 18° with 1 l. of a CCl_4 solution containing 0·01324 mol of I_2. The equilibrium concentration of I_2 in the CCl_4 layer was 0·007352 mol/l.; the distribution ratio of I_2 between CCl_4 and H_2O was 82·81. If the equilibrium constant of the reaction $KI_3 \rightleftharpoons KI + I_2$, $[KI][I_2]/[KI_3]$, = 0·001153 at 18°, calculate x.

5. Calculate the percentage hydrolysis of p-toluidine sulphate and the basic dissociation constant of p-toluidine from the following measurements. A litre of p-toluidine sulphate solution, containing 0·03132 mol of salt, was shaken with 59 c.c. of C_6H_6 and the concentration of base in the latter layer was 1·536 mol/l. The distribution ratio of p-toluidine between C_6H_6 and water is 24·1 at 25°; $K_w = 1·2 \times 10^{-14}$.

6. The distribution coefficient of hydroxyazobenzene between C_6H_6 and water is 539 at 25°. 1 l. of water containing 0·01 mol of hydroxyazobenzene and 0·01113 mol of $Ba(OH)_2$ was shaken with 60 c.c. C_6H_6. 50 c.c. of the C_6H_6 layer were found to contain 0·0954 g. of hydroxyazobenzene. Calculate the dissociation constant of hydroxyazobenzene as an acid, given $K_w = 1·2 \times 10^{-14}$ at 25°.

7. A solution of citric and acetic acids containing insufficient base for complete neutralization was shaken with $CHCl_3$. The latter was found to contain 0·0070 g. equivalent of acetic acid per l. and the water layer contained 0·300 g. equivalent of NaOH, 0·3049 g. equivalent of acetic and 0·3015 g. equivalent of citric acids, per l. If the distribution ratio of acetic acid C_{water}/C_{CHCl_3} is 26·4, show that citric and acetic acids compete for the base in the ratio 3 : 2.

8. a g. mol of Et acetate are dissolved in a mixture of v_1 vol. of dilute HCl and v_2 vol. of C_6H_6. As the ester hydrolyses in the acid layer fresh quantities are withdrawn from the C_6H_6 layer. The partition coefficient of the ester between C_6H_6 and water is $C = 0·079$. Show that the velocity constant is given by

$$k = 1/t \cdot (v_2 + v_1 C)/v_1 C \cdot \log a/(a - x).$$

98·6 c.c. of $0.10305N$ HCl were shaken with an equal vol. of $N/10$ Et acetate solution in benzene. The acid in the water layer required 107·85 c.c. of $N/10$ Ba(OH)$_2$ for complete neutralization after 2 hr., 113·3 c.c. after 4 hr., and 124·61 c.c. after 8 hr. Show that these figures are in agreement with the above equation.

9. A solution containing w_0 g. of solute in x c.c. is extracted n times with v c.c. of a given solvent. Show that the weight of solute remaining unextracted is

$$w = w_0\{kx/(kx + v)\}^n, \quad \ldots \quad (153)$$

where k is the distribution coefficient of the solute between the original solvent and the extracting liquid.

10. A substance exists in the normal state in phase A, and is associated n-fold in phase B. Show that the partition coefficient is $c_1/[c_2(1 - \beta)]^{1/n}$, where β is the degree of dissociation of the n-fold mols and c_1, c_2 are the total concentrations in the phases A and B respectively.

CHAPTER V

Electrochemistry

(a) CONDUCTIVITY OF ELECTROLYTES

(1) Definitions.

The strength of the current, i amperes, passing through any conductor of resistance r ohms, is related to the potential difference (P.D.) between the ends of the conductor, E volts, by *Ohm's law*,

$$i = E/r. \quad \ldots \quad (154)$$

One ampere deposits 0·001118 g. Ag in 1 sec. The *quantity* of electricity, W, passing any cross-section of the conductor in t sec. is, in *coulombs* (i.e. amperes × seconds),

$$W = it, \quad \ldots \quad (155)$$

and the heat developed is

$$Q = WE = Eit = i^2rt, \quad \ldots \quad (156)$$

where Q is expressed in volt-coulombs, or *joules* (1 joule = 0·23901 cal.).

The resistance of the conductor is proportional to its length,

l cm., and inversely proportional to its cross-section, s cm.^{2}, i.e

$$r = \rho l/s, \quad \ldots \ldots \quad (157)$$

where ρ is a constant, the *resistivity* (*specific resistance*) of the conductor. ρ is the resistance between two parallel faces of a cm. cube (*not* one cubic cm.) of the material. The reciprocal of the resistance is called the *conductance*. The *conductivity* (*specific conductance*, generally called *specific conductivity*) is given by $\varkappa = 1/\rho$. If ρ is in ohms, $\varkappa$ is in *reciprocal ohms*, or *mhos*.* It is the current in amp. between two parallel faces of a cm. cube of material between which the P.D. is 1 volt.

When the conductor is a solution, ρ is the resistance between electrodes 1 cm. $\times$ 1 cm. in area and 1 cm. apart. In practice, for any cell a factor is obtained (*cell constant*) by carrying out measurements on a solution of known conductivity. Then the observed conductance $\times$ cell constant $=$ specific conductance, $\varkappa$.

If v c.c. of the solution contain 1 mol of solute, or v' c.c. 1 g. equivalent, then the *molecular conductivity* is

$$\mu = \varkappa v, \quad \ldots \ldots \quad (158)$$

and the *equivalent conductivity*,

$$\Lambda = \varkappa v'. \quad \ldots \ldots \quad (159)$$

(2) Degree of Dissociation (Ionization), x.

If Λ_∞ (or Λ_0) is the equivalent conductivity of an electrolyte at infinite dilution (zero concentration), then

$$x = \Lambda/\Lambda_\infty = \Lambda/\Lambda_0. \quad \ldots \quad (160)$$

The value of Λ_∞ is obtained by graphical extrapolation or from formulæ. Kohlrausch proposed the function

$$\Lambda = \Lambda_\infty - a\,c^{1/3}, \quad \ldots \ldots \quad (161)$$

where a is a constant for a given salt at a given temperature. When $c = 0 \cdot 002$ equivalent/l. or less the equation

$$\Lambda = \Lambda_\infty - u\,c^{1/2} \quad \ldots \ldots \quad (162)$$

* Inserting the units in (157) we have: [ohms] $= \rho$[cm.]/[cm.^{2}] $= \rho$/[cm.], so that ρ is expressed in ohms $\times$ cm. The true dimension of $\varkappa$, therefore, is ohm^{-1}cm.$^{-1}$. As a rule the cm.$^{-1}$ is dropped, but it must be clearly understood that ohm^{-1} alone is not the true unit of conductance.

holds better. According to the Debye-Hückel theory of inter-ionic attraction, u is given by $\sqrt{2}\Lambda_\infty B$ where $B = [(K_1 w_1/D^{3/2}) + (K_2 b/D^{1/2})]$, where K_1, K_2 are universal constants for all solvents varying only with T, D = dielectric constant of solvent, $2w_1 = (l_a/l_k + l_k/l_a)$, and b is the harmonic mean of the ionic radii. Extrapolation of the $(\Lambda - \log c)$ curve is also used. Noyes proposed the equation

$$. \quad (163)$$

which is based on Storch's equation; n is usually 1·5, but the best value is found by trial for a given set of figures, the plot of Λ^{-1} against $(c\Lambda)^{n-1}$ being a straight line.

EXAMPLES.—1. A 70 per cent H_2SO_4 solution (by weight) has $d = 1·6146$ at 18° and $\varkappa_{18} = 0·2157$ ohm^{-1}. Calculate Λ and μ.

In a 70 weight per cent solution of H_2SO_4 there are 70 g. of acid in 100 g. of solution or 100/1·6146 c.c. of solution. The equivalent weight of H_2SO_4 is $\frac{1}{2} \times 98 = 49$, so that the vol. of solution containing 1 g. equivalent of acid $= 49 \times 100/1·6146 \times 70 = 43·36$ c.c. Hence $\Lambda = 0·2157 \times 43·36 = 9·35$ *ohms*$^{-1}$. The vol. of solution containing 1 mol of H_2SO_4 = $98 \times 100/1·6146 \times 70 = 86·72$ c.c. Hence $\mu = 0·2157 \times 86·72 = 18·7$ *ohms*$^{-1}$.

2. 7·329 g. of alcohol were evaporated at the boiling temperature, 78·2°, in 22 min. 54 sec. by the passage of 0·741 amp. through a Pt resistance of 8·796 ohms immersed in the alcohol. Calculate the latent heat of evaporation per g. of alcohol.

From (182) $Q = i^2 rt = (0·741)^2 \times 8·796 \times 1374 = 6636$ joules $= 6636 \times 0·239$ cal. $= 1586$ cal. This heat evaporated 7·329 g.; hence $L_e = 1586/7·329 = 216·4$ *cal./g.*

3. Using the method of Noyes, calculate Λ_∞ for NaF at 18° from the following values of Λ_c (c = g. equiv./l.):

c	=	0·02	0·01	0·005	0·001
Λ_c	=	81·1	83·48	85·25	87·84

The equation of Noyes is $\Lambda^{-1} = \Lambda_\infty{}^{-1} + (c\Lambda)^{n-1}/K\Lambda_\infty$. The value of n has to be found by trial; Λ^{-1} is plotted against $(c\Lambda)^{n-1}$ for various values of n, that value being finally chosen which best makes the experimental points lie on a straight line. A very short trial shows that $n = 1·5$ fits the first three measurements very well. The intercept of this line on the Λ^{-1} axis is seen to be 0·0111, whence $\Lambda_\infty = (0·0111)^{-1} = 90·1$ *ohm*$^{-1}$. The accepted value is 90·15.

EXERCISES.—XXV

1. The specific conductivity of a 0·5N KF solution is 0·0413 ohm^{-1} at 18°. If Λ_∞ is 111·35, calculate the concentration of the F ions in the solution.

2. A 50 per cent solution of NaOH ($d = 1\cdot527$) has $\kappa = 820 \times 10^{-4}$ ohm^{-1} at 18°. Calculate the value of Λ.

3. A conductivity cell has horizontal circular Pt electrodes of diameter 1·34 cm. and 1·72 cm. apart. The cell is filled with $0\cdot05N$ NaNO$_3$ solution. If a P.D. of 0·5 volt between the electrodes causes 1·85 milliamps. (= thousandths of an amp.) to flow through the solution, calculate Λ and $\varkappa$. Temperature = 18°.

4. The cell in Exercise 3 was filled with $N/50$ KCl ($\varkappa = 0\cdot002397$ ohm^{-1} at 18°) and its resistance, as measured by a Wheatstone bridge, was found to be 515·6 ohms. Calculate Λ for the NaNO$_3$ solution from the data of the preceding question. (This result will be more accurate than that of Exercise 3. Why?)

5. 10·032 g. of C$_6$H$_6$ at 79·5°, the boiling temperature under the
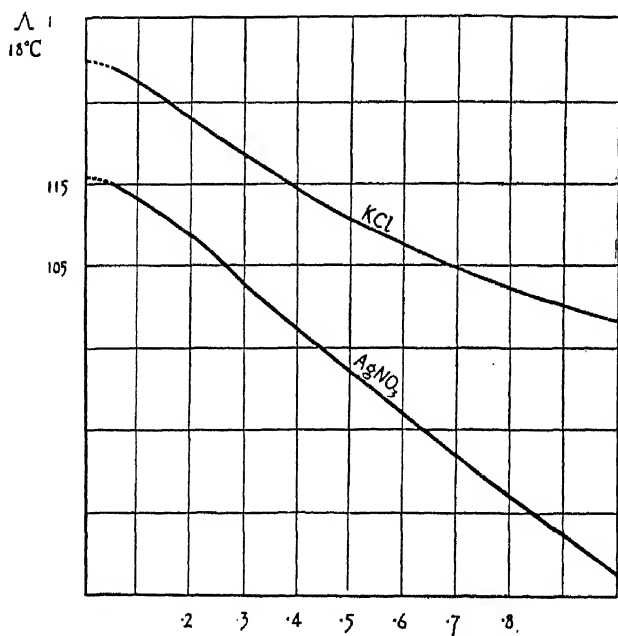
Fig. 5.—Conductivity Curves

conditions of the experiment, evaporated in 8 min. 57 sec. when heated by a current of 1 ampere passing through a Pt spiral of $r = 7\cdot4335$ ohms immersed in it. Calculate the heat of evaporation per g. at 79·5°.

6. In an experiment to find the heat of fusion of monoclinic S, 9·513 g. of the latter, initially at 4·17° below the m.p., were fused by the passage of 0·998 amp. for 392·2 sec. through a wire of $r = 3\cdot56$ ohms embedded in the S. The specific heat of monoclinic S is 0·22

cal./g., independent of t near the m.p. If the water value of the calorimeter was 53·98, calculate L_f for S at the m.p.

7. Calculate Λ_∞ for $AgNO_3$, using the $\Lambda - c^{\frac{1}{2}}$ curve, from the following equivalent conductivities at 18° (c = g. equiv./l.):

$c = 1$ 0·5   0·1   0·01   0·005   0·0005   0·0002   0·0001
$\Lambda = 67·6$ 77·5   94·33   107·81   110·04   113·89   114·56   115·01

See fig. 5.

8. Calculate Λ_∞ for $AgNO_3$, using the $\Lambda - \log c$ curve; data in previous exercise. See fig. 6.

9. Calculate Λ_∞ for KCl at 18°, according to the $\Lambda - c^{\frac{1}{2}}$ and
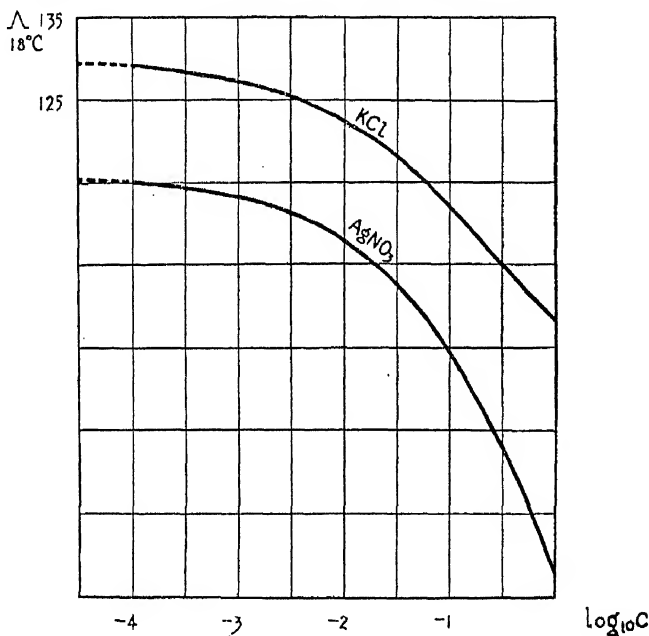
Fig. 6.—Conductivity Curves

$\Lambda - \log c$ curves, from the following equivalent conductivities (c = g. equiv./l.):

$c = $ 0·5   0·1   0·05   0·01 0·005 0·002 0·001   0·0005 0·0002 0·0001
$\Lambda = 102·4$ 112·0 115·8 122·4 124·4 126·3 127·3 128·1   128·8 129·1

See figs. 5 and 6.

10. By extrapolating the $\Lambda - c^{\frac{1}{2}}$ curve, determine Λ_∞ for NaCl at 18° (c = mol/l.):

$c = $ 0·005   0·002   0·001   0·0005   0·0002   0·0001
$\Lambda = 103·78$ 105·55   106·49   107·18   107·82   108·10

11. Calculate Λ_∞ for $TlNO_3$ solution at 18°, using Noyes' method (c = concentration in g. equiv./l.):

c	=	0·0005	0·0002	0·0001
Λ	=	125·60	126·29	126·62

(3) Faraday's Laws.

If m g. of ion are liberated in t sec. by a current of i amperes, then

$$m = kit = zit/F, \quad . \quad . \quad . \quad (164)$$

where k is the *electrochemical equivalent* and z the chemical equivalent of an ion, and F is a universal constant, the *faraday* or *equivalent of electricity*. One coulomb liberates k g. of ion and F coulombs liberate z g. The value of $F = 96,500$ coulombs/equivalent. Exact at. wts. should be used in problems involving Faraday's laws.

(4) Ionic Mobilities.

According to Kohlrausch, for infinitely dilute solutions:

$$\Lambda_\infty = {}_\infty l_k + {}_\infty l_a, \quad . \quad . \quad . \quad (165)$$

where ${}_\infty l_k$ and ${}_\infty l_a$ are the *mobilities*, in ohm^{-1}, of the kation and anion, respectively. They are proportional to the actual velocities, u and v, of the ions, in cm./sec. under a potential gradient of 1 volt/cm.: $l = $ constant $\times u$. Now l has the dimensions of Λ (from 165), i.e. ohm^{-1} cm.$^{-1}$ $\times$ cm.^{3}/g. equivalent. Also $u = $ (cm./sec.)/(volt/cm.) $=$ cm.^{2}/volt $\times$ sec. Hence the proportionality constant $= l/u = $ sec. $\times$ amp./g. equivalent $=$ coulombs/g. equivalent $= F$ (from 164). Hence:

$$uF = {}_\infty l_k \text{ and } vF = {}_\infty l_a, \quad . \quad . \quad (166)$$

or $\quad u = \qquad\qquad\qquad\qquad {}_\infty^; l_a. \quad (166a)$

If u' and v' are the velocities in cm./sec. under a potential gradient of 1 C.G.S. unit, the numerical factor is $1·036 \times 10^{-13}$: $u' = 1·036 \times 10^{-13} {}_\infty l_k$, &c.

The *temperature coefficient* of a univalent ion of mobility l is given by $0·0136 + 0·67/(18·5 + l)$.

(5) Transport (or Transference) Numbers.

Since u amd v are not usually equal, the current transported is shared unequally by the ions. The fraction of the total current carried by an ion is the *transport* or *transference* number of the ion. If n is the transport number of the anion, $1 - n$ is that of the kation, and by definition

$$n = l_a/(l_k + l_a); \quad 1 - n = l_k/(l_k + l_a). \quad . \quad (167)$$

The determination of transport numbers is often carried out by electrolysing between " soluble " electrodes a dilute solution of an appropriate salt. From (166) and (167), $n = constant \times v$; and since v is proportional to the fall in concentration, Δc, of the anion in the electrode compartment which it is *leaving*, $n = constant \times \Delta c$. Now if the anion carried *all* the current, Δc would be the amount (A) of anion equivalent to the total current (measured in a coulometer) and n would be unity; so that $constant = 1/A$. Hence $n = constant \times \Delta c$
$\Delta c / A$

(6) Diffusion of Electrolytes.

According to Nernst the *diffusion coefficient*, D, of an electrolyte is given by

$$D = 2u'v' \, RT/(u' + v'). \quad . \quad . \quad (168)$$

Units.—On the absolute scale D is the quantity of salt (expressed on the same scale as the concentration) which will migrate per second through a cross-section of 1 cm.[2] where the concentration difference per centimetre is unity. The c.c. must be taken as unit of vol. and unit quantity of ions will be associated with the C.G.S. unit quantity of electricity. If Λ_∞ is in C.G.S. units (1 ohm = 10^9 C.G.S. units) and if unit quantity of electricity is associated with v equivalents of ion, then (166) may be written $u' + v' = (l_k + l_a)v10^{-9}$, so that $D = 2l_k \, l_a \cdot vRT10^{-9}/(l_k + l_a)$. Now v equivalents of ion in 1 c.c. exert an osmotic pressure of $22,412 v$ atm. = $22,412 \times 1,013,225 v$ dynes/cm.[2] = $2 \cdot 2705 \times 10^{10} v$ dynes/cm.[2]. For univalent ions $v = 1/9650$ in the C.G.S. system (1 amp. = 10^{-1} C.G.S. units), hence, at any temperature T, the pressure = $2 \cdot 2705 \times 10^{10} \times T/273 \times 9650 = 2 \cdot 3525 \times 10^6 T/273 = RT$. Hence in absolute units $D = 2l_k \, l_a \, v/(l_k + l_a) \cdot (0 \cdot 002353 \, T$

/273).   To convert to practical units (amount per day) D must be multiplied by 8.64×10^4 (= number of seconds in a day). At $t°$ C. the above equation may be written for uni-univalent salts:

$$D \text{ (per day)} = 0.04485 l_k\, l_a /(l_k + l_a) . [1 + 0.0034(t - 18)].$$

EXAMPLES.—1. A current of 1·7 amperes was passed for 1 hr. through a solution of $AgNO_3$; 10·68 g. of salt were decomposed. Calculate the current efficiency.

From (164), since $z = 107.88$, $k_{\mathrm{Ag}} = 107.88/96,500$. Hence, mass of Ag liberated is $m = 107.88 \times 1.7 \times 60 \times 60/96,500$ g. But 107·88 g. of Ag $\equiv$ 169·88 g. of $AgNO_3$; weight of salt decomposed = $169.88 \times 1.7 \times 60 \times 60/96,500 = 10.78$ g.   The weight decomposed in practice was 10·68; hence current efficiency = $10.68/10.78 = 0.991$ or *99·1 per cent.*

2. From the following values of Λ_∞ at 18° calculate that for $NaIO_3$: KIO_3, 98·54; KF, 111·54; NaF, 90·08.

From equation (165), $_\infty l_{\mathrm{K}} + _\infty l_{\mathrm{IO_3'}} = 98.54$. Let $_\infty l_{\mathrm{Na}\cdot} + _\infty l_{\mathrm{IO_3'}} = \Lambda_\infty\,{}_{\mathrm{NaIO_3}} = x$. Then $_\infty l_{\mathrm{K}} - _\infty l_{\mathrm{Na}\cdot} = 98.54 - x$. But $_\infty l_{\mathrm{K}} + _\infty l_{\mathrm{F'}}$ 111·54, and $_\infty l_{\mathrm{Na}\cdot} + _\infty l_{\mathrm{F'}} = 90.08$, so that $\cdot - _\infty l_{\mathrm{Na}\cdot} = 21.46$, or $21.46 = 98.54 - x$, whence $x = 77.08$.

3. The apparent ionic mobilities of Na and NO_3 in $N/10$ $NaNO_3$ solution are 36·4 and 50·8; $\Lambda_\infty = 105.3$. Calculate the apparent and real velocities of the ions.

The " apparent " mobilities and velocities are due to the incomplete dissociation of the salt. Substituting in (166), for the apparent velocity we have $\alpha u = 50.8/96,500 = 0.0005265$ cm./sec., and the real velocity $= u = 0.0005265/\alpha = 0.0005265 \times 105.3/(36.4 + 50.8) = 0.0006357$ cm./sec. Similarly for the Na· ion we have: apparent velocity $= 0.0003773$ cm./sec. and real velocity $= 0.0001555$ cm./sec.

4. A solution of $NaPO_3$, 25·1998 g. of which contained 0·1755 g. of P_2O_5, was electrolysed in a transport apparatus with a soluble anode. After the experiment, the anode solution, which weighed 91·6632 g., contained 0·7370 g. of P_2O_5, whilst 0·2626 g. of Ag was deposited in a coulometer in series with the apparatus. Calculate the transport number of the Na· ion in the solution.

(i) After electrolysis: 91·6632 g. of solution $\equiv 204.08 \times 0.7370/142.08 = 1.0586$ g. of $NaPO_3$; $\therefore$ 91·6632 $-$ 1·0586 $= 90.6046$ g. of water are associated with 1·0586 g. of $NaPO_3 = 1.0586 \times 79.04/102.04 = 0.81999$ g. of PO_3'.

(ii) Before electrolysis: 25·1998 g. of solution $\equiv 0.1755$ g. of $P_2O_5 \equiv 0.1755 \times 204.08/142.08 = 0.2521$ g. of $NaPO_3$; $\therefore$ 25·1998 $- 0.2521 = 24.9477$ g. of water were associated with $0.2521 \times 79.04/102.04$ g. of PO_3'; and $\therefore$ 90·6046 g. of water were associated with $0.2521 \times 79.04 \times 90.6046/102.04 \times 24.9477 = 0.70923$ g. of PO_3'.

Hence during the electrolysis the PO_3' concentration has increased by $0.81999 - 0.70923 = 0.11076$ g. of PO_3'. But this concentration increase has occurred at the anode; Na· ions are moving away, leaving

PO_3' ions behind, which, however, are combining with the anode ("soluble" anode) and remaining in solution. Hence this increase in PO_3' concentration is a measure of the decrease in $Na^.$ concentration $\therefore$ fall in $Na^.$ concentration at anode $\equiv 0\cdot 11076$ g. of PO_3'.

(iii) Since $107\cdot 88$ g. of $Ag \equiv 79\cdot 04$ g. of PO_3', then $0\cdot 2626$ g. of $Ag \equiv 79\cdot 04 \times 0\cdot 2626/107\cdot 88 = 0\cdot 19240$ g. of PO_3'.

(iv) Hence, transport number of $Na^. = 0\cdot 11076/0\cdot 19240 = 0\cdot576$.

5. A solution containing $8\cdot 108$ per cent of KCl and $4\cdot 418$ per cent of raffinose was electrolysed in a transport apparatus, $0\cdot 04974$ equivalent of electricity passing through. At the end of the experiment the anode portion weighed $103\cdot 21$ g. and contained $6\cdot 510$ per cent of KCl and $4\cdot 516$ per cent of raffinose. Assuming the raffinose to remain stationary during the experiment, calculate the true transport number of $K^.$. (N.B.—Ions are assumed to be hydrated and their transference to be accompanied by transference of water. A reference substance other than water is therefore used, viz. raffinose. Transport numbers calculated with reference to some inert substance other than the solvent are called "true" transport numbers.)

100 g. of solution contain after the experiment $6\cdot 510$ g. of KCl and $4\cdot 516$ g. of raffinose; hence the anode solution, weighing $103\cdot 21$ g., contains $6\cdot 719$ g. of KCl and $4\cdot 661$ g. of raffinose. Before electrolysis, however, $8\cdot 108$ g. of KCl were associated with $4\cdot 418$ g. of raffinose, i.e. $8\cdot 108 \times 4\cdot 661/4\cdot 418 = 8\cdot 553$ g. of KCl were associated with $4\cdot 661$ g. of raffinose. Hence the concentration decrease $= 8\cdot 553 - 6\cdot 719 = 1\cdot 834$ g. of KCl $= 1\cdot 834 \times 39/74\cdot 5$ g. of $K^.$. If the $K^.$ had carried all the current the transference would have been $39 \times 0\cdot 04974$ g. Hence the required transport number $= 1\cdot 834 \times 39/74\cdot 5 \times 39 \times 0\cdot 04974 = 0\cdot495$.

EXERCISES.—XXVI

1. $33\cdot 488$ g. of palmitic acid were fused at the m.p. by the passage of $1\cdot 55$ amp. through a Pt spiral of $r = 1\cdot 41$ ohms embedded in the acid. If $1\cdot 0758$ g. of Cu were simultaneously deposited from $CuSO_4$ solution in a voltameter in series with the spiral, calculate the heat of fusion per g. of acid.

2. From the following values of Λ_∞ calculate Λ_∞ for $LiIO_3$: $LiNO_3$, $95\cdot 18$; KIO_3, $98\cdot 49$; KNO_3, $126\cdot 5$.

3. For KCl solution at $0° \Lambda_\infty = 81\cdot 4$, the transport number of the kation being $0\cdot 493$. Show that the mobility of the I' ion is $43\cdot 4$ at $0°$ if Λ_∞ for KI is $83\cdot 5$ at this temperature.

4. If the specific conductivity of pure water is $0\cdot 04 \times 10^{-6}$ ohm^{-1} at $18°$, and if $_\infty l_{\text{H}^.} = 315$ and $_\infty l_{\text{OH}'} = 174$, find the hydrogen-ion concentration.

5. The value of Λ at $18°$ for NaOH solutions between concentrations of $N/30$ and $N/1000$ is given by $\Lambda = 217 - 75\cdot 7\sqrt{c}$, c being the concentration in g. mol./l. If the mobility of the $Na^.$ ion is $43\cdot 4$ at $18°$, what is that of the OH' ion at this temperature?

6. The specific conductivity of supersaturated $BaSO_4$ solution, containing $0\cdot 0040$ g. of salt in 400 c.c., is 85×10^{-6} ohm^{-1}, whilst

that of a saturated solution is 20×10^{-6} ohm^{-1}. The temperature is $18 \cdot 3°$. Calculate the solubility of $BaSO_4$ at this temperature.

7. The specific conductivity of saturated $PbCrO_4$ solution is $0 \cdot 1 \times 10^{-6}$ ohm^{-1} at $18°$. The mobilities of the ions are $\frac{1}{2}Pb^{\cdot\cdot}$ 61, $\frac{1}{2}CrO_4''$ 72, at infinite dilution. Calculate the solubility of $PbCrO_4$ at $18°$ in g./l.

8. If Λ_∞ for $CaCl_2$ is $116 \cdot 75$ at $18°$ and if the transport number of Cl' is $0 \cdot 562$ in very dilute solution, calculate the velocity of $Ca^{\cdot\cdot}$ in cm./sec. under unit potential gradient.

9. The velocity of migration of the $K^{\cdot}$ ion at $25°$ is $0 \cdot 0007751$ cm./sec., and that of the I' ion, $0 \cdot 0007929$ cm./sec., both under unit potential gradient. The equivalent conductivity of KI solution $(v = 256 \text{ l./mol})$ is $147 \cdot 1$ at $25°$. What is the degree of dissociation of the salt in this solution?

10. A solution of $CdSO_4$ containing $11 \cdot 5597$ g. of salt in 100 g. of solution was electrolysed at $10°$ between Cd electrodes, and after the experiment the anode solution, which weighed $171 \cdot 658$ g., was found to contain $20 \cdot 7225$ g. of the salt. $1 \cdot 8688$ g. of Ag were deposited in a coulometer in the circuit. Calculate the transport number of Cd.

11. A solution of $10 \cdot 057$ g. of $CuSO_4$ in 100 g. of solution was electrolysed between Cu electrodes in a transport apparatus. After electrolysis $54 \cdot 565$ g. of the anode solution contained $5 \cdot 726$ g. of $CuSO_4$ and $0 \cdot 5008$ g. of Ag had been deposited in a coulometer in the circuit. Calculate the transport number of $Cu^{\cdot\cdot}$ in the solution.

12. A solution of LiCl containing $0 \cdot 074$ per cent of Cl was electrolysed in a suitable transport apparatus. When $0 \cdot 4789$ g. of Ag had been deposited in the coulometer the anode liquid, which weighed $332 \cdot 104$ g., was found to contain $0 \cdot 10557$ per cent of Cl. Calculate the transport number of Li.

13. A solution of HNO_3 containing $0 \cdot 05922$ milli-equivalents of acid per g. was electrolysed in a transport apparatus. After electrolysis the kathode portion, which weighed $214 \cdot 08$ g., required $107 \cdot 72$ g. of $Ba(OH)_2$ solution containing $0 \cdot 11064$ milli-equivalents of alkali per g. for neutralization. In the coulometer $523 \cdot 2$ mgm. of Ag were deposited. Calculate the transport number of the anion.

14. Calculate the composition of the salt formed by dissolving equivalent amounts of KI and CdI_2 in water from the following migration data. $15 \cdot 8994$ g. of such a solution yielded on analysis $16 \cdot 102$ g. of AgI, $3 \cdot 4367$ g. of KNO_3 and $2 \cdot 223$ g. of CdO. After the experiment the kathode portion of the solution weighed $24 \cdot 6033$ g. and yielded $24 \cdot 6147$ g. of AgI, $6 \cdot 2027$ g. of KNO_3, and $2 \cdot 8352$ g. of CdO. During the experiment $0 \cdot 9784$ g. of Ag was deposited in the coulometer.

15. A solution containing $6 \cdot 344$ per cent of NaCl and $4 \cdot 449$ per cent of raffinose was electrolysed between " soluble " electrodes, $0 \cdot 0629$ equivalents of electricity being passed. At the end of the experiment the anode solution weighed $78 \cdot 13$ g. and contained $4 \cdot 731$ per cent of KCl and $4 \cdot 584$ per cent of raffinose. Calculate the true transport number of $Na^{\cdot}$.

16. Calculate the true transport number of the $Li^{\cdot}$ ion from the

following results. A solution containing 4·939 per cent of LiCl and 4·730 per cent of raffinose was electrolysed between soluble electrodes, 0·04643 equivalents of electricity passing through the cell. The kathode solution weighed 81·47 g. after the experiment and contained 5·565 per cent of LiCl and 4·619 per cent of raffinose.

(b) EQUILIBRIUM IN SOLUTION

(1) Ostwald's Dilution Law.

The application of the law of mass action to a dilute solution of a binary electrolyte, ionized to the extent x, and of concentration c mol/l., gives the equation

$$x^2c/(1-x) = c\Lambda^2/\Lambda_\infty(\Lambda_\infty - \Lambda) = K, \quad . \quad (169)$$

or
$$x = [(1 + 4c/K)^{1/2} - 1]K/2c, \quad . \quad (169a)$$

where K is the *dissociation* or *ionization constant*. When x is very small (169) becomes $x = \sqrt{K/c}$. The equation may be written: $\Lambda c = K\Lambda^2_\infty \Lambda^{-1} - K\Lambda_\infty$, a linear relation between Λc and Λ^{-1}.

The dilution law fails in the case of strong (highly ionized) electrolytes, to which Storch's equation: $c^n x^n/c(1-x) = constant$, may be applied.

Equation (135) also holds for solutions obeying (169). Q then represents the *heat of dissociation* of the solute in the solution.

(2) Isohydric Principle. Conductivity of Mixed Electrolytes.

In a mixture of two salts with a common ion, each salt has a degree of dissociation equal to that which it has when present alone in a solution in which its ions have a concentration equal to the concentration of the common ion in the mixture.

Let two solutions of electrolytes having vols. v_1 and v_2, containing n_1, n_2 g. equivalents of electrolyte per c.c., be mixed. Let the vol. after mixing $= p(v_1 + v_2)$. Let the ionizations *after* mixing be x_1 and x_2. Then

$$p(v_1 + v_2)x = [x_1 n_1 v_1 (\Lambda_\infty)_1 + x_2 n_2 v_2 (\Lambda_\infty)_2]. \quad (170)$$

Values of x_1 and x_2 may be computed graphically on the assumption of the isohydric principle (*Arrhenius's method*) or may be calculated on the assumption that the ionization of each

salt is equal to that which it has when present alone at a con-
centration equal to the total concentration of the mixture
(*Barmwater's method*).   Thus from (160) and (161) we have
$1 - x = k'c^{1/3}$, where $k' = a/\Lambda_\infty$, a constant for a given salt
at a given temperature.   By applying the second assumption
we find $1 - x_1 = k_1'(c_1 + c_2)^{1/3}$ and $1 - x_2 = k_2'(c_1 + c_2)^{1/3}$,
and x_1, x_2 can be calculated.   Barmwater's principle may also
be applied with Storch's equation.

(3) Solubility Product.

A saturated solution of a sparingly soluble electrolyte,
$A_x B_y$, in contact with the solid salt may be regarded as com-
pletely dissociated, and the law of mass action gives

$$[xA^\cdot]^x\,[yB']^y = x^x\,y^y\,s^{(x+y)} = K\,[A_x\,B_y] = L, \quad (171)$$

where L, the *solubility product*, is a constant at any parti-
cular temperature, and s is the molecular solubility of the salt.
Systems always adjust themselves, if possible, so that the
ionic products for the separate salt constituents equal the
respective solubility products.

(4) Hydrolysis of Salts.

Pure water is slightly ionized: $H^\cdot + OH' \rightleftharpoons H_2O$; hence,
according to the law of mass action, $[H^\cdot]\,[OH'] = K\,[H_2O]$
$= K_w$, the *ionization*, or *dissociation, constant of water*.

Salts of weak acids and bases are decomposed by water
with the formation of free (un-ionized) acid or base.

(i) *Salts of strong bases and weak acids*, e.g. $KCN + H_2O \rightleftharpoons$
$K^\cdot + OH' + HCN$.   From the law of mass action, the *hydro-
lysis constant*, K_h = [base] [acid] /[unhydrolysed salt].   If c is
the concentration of the salt, x the degree of hydrolysis, and
$K_a = [H^\cdot]\,[CN'] /[HCN]$, then $K_h = x^2c/(1 - x)$.   Also (172):
$K_h = K_w/K_a$ and

$$x = -\frac{K_w}{2cK_a} \pm \Big[\Big(\frac{K_w}{K_a}\Big)^2 \frac{1}{4c^2} + \frac{K_w}{cK_a}\Big]^{\frac{1}{2}}. \quad (172a)$$

When x is very small (K_a is large compared with K_w), then
$K_h = x^2c$.

(ii) *Salts of weak bases and strong acids*.   Equations (172) and
(172a) hold with K_a replaced by K_b ($= [B^\cdot]\,[OH']/[BOH]$).

(iii) *Salts of weak bases and weak acids.*—In these cases (173), $K_h = K_w/K_aK_b$, holds and $K_h = x^2/(1-x)^2$, showing that the degree of hydrolysis, x, of such salts is independent of the concentration.

EXAMPLES.—1. If the dissociation constant of propionic acid is $1 \cdot 3 \times 10^{-5}$ at $25°$, find the concentration of the solution having $[H^·] = 5 \times 10^{-3}$.

Let c = required concentration in mol/l. Then $K = [H^·][C_2H_5COO']/[C_2H_5COOH]$ or, since $[H^·] = [C_2H_5COO']$, $1 \cdot 3 \times 10^{-5} = (5 \times 10^{-3})^2/(c - 5 \times 10^{-3})$, whence $c = 1 \cdot 928 \ mol./l.$

2. One mol of NaOH is added to a solution containing 1 mol of HCOOH ($K_1 = 0 \cdot 000214$) and 1 mol of C_3H_7COOH ($K_2 = 0 \cdot 0000149$). Find the ratio in which the base distributes itself between the two acids.

Suppose in the mixed solution there are b mols of NaOH, c_1 mols of HCOOH, and c_2 mols of C_3H_7COOH. Let the fraction of HCOOH reacting with NaOH be x; then $(1-x)$ reacts with C_3H_7COOH, and there will be bx mols of HCOONa and $b(1-x)$ mols of C_3H_7COONa. Both salts are assumed completely ionized, giving rise to bx mols of H.COO' and $b(1-x)$ mols of C_3H_7COO', respectively. Now $K_1 = [H.COO'][H^·]/[HCOOH] = bx[H^·]/(c_1 - bx)$ and $K_2 = b(1-x)[H^·]/(c_2 - b + bx)$, whence $K_1/K_2 = x/(1-x) \cdot (c_2 - b + bx)/(c_1 - bx)$. In the present case $c_1 = c_2 = b = 1$, whence $K_1/K_2 = x^2/(1-x)^2$. The required ratio, therefore, is $\sqrt{K_1/K_2} = \sqrt{21 \cdot 4/1 \cdot 49} = 3 \cdot 8$, or $0 \cdot 79$ mol of NaOH unites with H.COOH and $0 \cdot 21$ mol with $C_3H_7.COOH$.

3. The equivalent conductivities, Λ, of NaCNS in EtOH at $25°$ are ($c = $ mol/c.c. $\times 10^4$):

$c =$	1·052	3·509	5·754	6·136	6·748	0
$\Lambda =$	21·5	15·95	13·75	13·48	13·15	54·83

The corresponding values for NaI are:

$c =$	20·33	18·91	17·62	17·41	17·01	0
$\Lambda =$	9·89	10·18	10·47	10·52	10·59	52·98

Calculate (i) by Barmwater's methods, and (ii) by Arrhenius's method the specific conductivity of a saturated alcoholic solution containing per c.c. $17 \cdot 62 \times 10^{-4}$ mol of NaI and $5 \cdot 754 \times 10^{-4}$ mol of NaCNS. (Assume the solutions obey Storch's equation.)

In both cases it is necessary to know the ionizations, x, at concentrations in the pure solutions greater than saturation. These are calculated by Storch's equation, $(cx)^n/c(1-x) = K$. First find the constants K and n by plotting $n \log(cx) - \log K$ against $\log c(1-x)$. The slope of this line is n and the intercept $-\log K$. For NaCNS, $n = 1 \cdot 54$ and $K = 27 \cdot 6 \times 10^{-4}$; for NaI, $n = 1 \cdot 63$ and $K = 16 \cdot 0 \times 10^{-14}$.

(i) *Barmwater's Method.*—According to this method the ionization

of the NaCNS (or NaI) in the mixture is equal to the value of the ionization of this salt in pure alcoholic solution of concentration $(17 \cdot 62 + 5 \cdot 754) \times 10^{-4}$ mol/c.c. To find x for NaCNS corresponding to this concentration, values of x are assumed (lower than those corresponding to the figures given above) and the corresponding values of c are found from the Storch equation. These values of x are plotted against the calculated values of c, and for NaCNS at $c = 23 \cdot 374 \times 10^{-4}$ mol/c.c., $x = 0 \cdot 1628$. Similarly, for NaI at the same concentration, $x = 0 \cdot 1776$. Hence $\varkappa = (0 \cdot 1776 \times 0 \cdot 001762 \times 52 \cdot 98) + (0 \cdot 1628 \times 0 \cdot 0005754 \times 54 \cdot 83) = 0 \cdot 02172$.

(ii) *Arrhenius's Method.*—First obtain the concentration c' of the common ion in the mixture. Plot on the same axes values of x against xc for the separate salts. Now $c' = 0 \cdot 001741 x_1 + 0 \cdot 0006136 x_2$, where x_1, x_2 are the ionizations of NaI and NaCNS in the mixture. Assume a value for c' (i.e. xc) and read from the graph the corresponding values of x_1 and x_2. Repeat this process until the above relationship is satisfied. It will be found that $xc = 4 \cdot 065 \times 10^{-4}$ and $x_1 = 0 \cdot 1798$, $x_2 = 0 \cdot 1557$. Hence $\varkappa = 0 \cdot 02170$.

4. Solutions of alkali formates in anhydrous formic acid obey the law of mass action. The constant at $25°$ for K formate is $1 \cdot 090$ and that for Na formate is $0 \cdot 810$. Calculate the specific conductivity of a solution of $0 \cdot 1622$ mol of Na formate ($\Lambda_\infty = 66 \cdot 23$) and $0 \cdot 05699$ mol of K formate ($\Lambda_\infty = 68 \cdot 92$) in 1 l. of solution.

From (170), $1000 \varkappa = x_1 c_1 (\Lambda_\infty)_1 + x_2 c_2 (\Lambda_\infty)_2$, c being in equivalent/l. For the respective salts we have (i): $x_1(x_1 c_1 + x_2 c_2)/(1 - x_1) = K_1$, and (ii): $x_2(x_1 c_1 + x_2 c_2)/(1 - x_2) = K_2$; ∴ (iii): $x_1 = (x_2 K_1/K_2)/ 1 - x_2(1 - K_1/K_2)$. Divide (ii) by x_2^2; (iv) $c_2 + c_1 x_1/x_2 = K_2(1 - x_2)/ x_2^2$, which is identical with the law of mass action (v): $c' = K_2(1 - x_2)/x_2^2$, where $c' = c_2 + c_1 x_1/x_2$ is the concentration of salt 2 in a pure solution in which its degree of dissociation is x_2. A series of arbitrary values of x_2 is taken, x_1 is calculated from (iii) and c' from (v); x_1/x_2 is then plotted against c'. A value of c' is estimated; the corresponding x_1/x_2 is read off and if it does not make $c_2 + c_1 x_1/x_2 = c'$ the process is repeated until it does. In the present case $c' = 0 \cdot 2115$ and x_1/x_2 (where " 2 " refers to the K salt) = $0 \cdot 953$. From (v) x_2 is calculated to be $0 \cdot 857$; hence $x_1 = 0 \cdot 8167$ and $\varkappa = 0 \cdot 01214$. This method is due to Schlesinger and Reed.

5. (i) What vols. and concentrations must be mixed in order to prepare 1 l. of mixed acetic and butyric acids ($K = 1 \cdot 9 \times 10^{-5}$ and $1 \cdot 48 \times 10^{-5}$ at $25°$, respectively) containing $0 \cdot 7$ mol of each acid, without altering the degrees of dissociation of the separate acids?

(ii) What concentrations and vols. would be required if the dissociation of acetic acid was to be depressed by 30 per cent of what it would have been in the mixture?

(i) Let c_1, c_2 be the concentrations of the weak acids HA_1 and HA_2, and x_1, x_2 the degrees of dissociation. After mixing, since the values of x are to remain unaltered, $[H \cdot] = (x_1 + x_2)/(v_1 + v_2)$ and $[A_1 \cdot] = x_1/(v_1 + v_2)$; ∴ $K_1 = (x_1 + x_2)x_1/(1 - x_1)(v_1 + v_2)$. But $K_1 = x_1^2/(1 - x_1)v_1$; by division, $x_2 c_2 = x_1 c_1$, which is the condition that the two acids may be mixed without change in degree of dissociation. If K_1 and K_2 are small, $1 - x_1 = 1 - x_2 = 1$ approx.

and $K_1/K_2 = (x_1c_1)^2/c_1 . c_2/(x_2c_2)^2 = c_2/c_1$. To solve the first part of the problem, then, three equations have to be solved: $v_1 + v_2 = 1$; $c_1v_1 = c_2v_2 = 0.7$, and $1.48 \times 10^{-5}/1.9 \times 10^{-5} = 0.779 = c_2/c_1$, where v_1 and v_2 are the vols. (in l.) that have to be mixed. It is found that 437.9 c.c. of butyric acid containing 1.598 mol/l. have to be mixed with 562.1 c.c. of acetic acid of concentration 1.246 mol/l.

(ii) Let y_1, y_2 be the degrees of dissociation if each acid, separately, occupied the total vol. of the mixture. Let β_1, β_2 be the actual degrees of dissociation in the mixture. Then the concentration of the common ion is $\beta_1c_1 + \beta_2c_2$ and so $K_1 = y_1^2c_1/(1-y_1) = \beta_1c_1(\beta_1c_1 + \beta_2c_2)/(1 - \beta_1)c_1$. With the analogous expression for c_2 this gives $K_1/K_2 = \beta_1/(1 - \beta_1) . (1 - \beta_2)/\beta_2 = \beta_1/\beta_2$ when K_1 and K_2 are small. Hence $K_1 = y_1^2c_1/(1 - y_1) = \beta_1^2c_1[1 + (K_2/K_1)(c_2/c_1)]/(1 - \beta_1)$, or, if y_1 and β_1 are very small,

$$y_1/\beta_1 = [1 + (K_2/K_1)(c_2/c_1)]^{\frac{1}{2}}. \quad . \quad . \quad (174)$$

Similarly $\qquad y_2/\beta_2 = [1 + (K_1/K_2)(c_1/c_2)]^{\frac{1}{2}}.$

If the degree of dissocation of acetic acid is to be depressed 30 per cent, $\beta_1 = 0.7y_1$ and $y_1/\beta_1 = 1/0.7$, whence $c_2/c_1 = 1.336$. As before $c_1v_1 = c_2v_2 = 0.7$ and $v_1 + v_2 = 1$. It is found that 571.9 c.c. of acetic acid of concentration 1.224 mol/l. have to be mixed with 428.1 c.c. of butyric acid of concentration 1.635 mol/l.

The ratio of the degree of dissociation of the butyric acid before and after is given by $y_2/\beta_2 = [1 + (1.9/1.48)(1/1.336)]^{\frac{1}{2}} = 1.4$, i.e. it is depressed about 29 per cent.

6. The solubility of cinnamic acid ($K = 3.55 \times 10^{-5}$) is 0.00331 mol/l. in pure water at 25° and 0.00804 mol/l. in a solution containing 0.01 mol of aniline. An aniline-cinnamic acid complex is present in solution which may be regarded as being dissociated to the same extent as LiCl at the same dilution, 93 per cent for a concentration of 0.00506 mol/l. If $Kw = 1.3 \times 10^{-14}$, calculate the dissociation constant of aniline.

According to (169), $0.00331\alpha^2/(1 - \alpha) = 3.55 \times 10^{-5}$ or $\alpha = 0.0984$. Hence concentration of undissociated acid $= 0.00331 (1 - \alpha) = 0.002984$ mol/l. In presence of 0.01 mol of aniline the solubility of cinnamic acid $= 0.00804$ mol/l. Hence concentration of acid present partly as free ions and partly as the aniline compound is $0.00804 - 0.00298 = 0.00506$ mol/l. The concentration of undissociated compound $= 7$ per cent of $0.00506 = 0.000354$ mol/l. and the concentration of free acid anions $= 0.00506 - 0.00035 = 0.00471$; $\therefore [H^.] = 3.55 \times 10^{-5} \times 0.00298/0.00471 = 0.0000225$ mol/l. Hence the concentration of free base kations $= 0.00471 - 0.00002 = 0.00469$ mol/l., and the concentration of undissociated base $= 0.01 - 0.00468 - 0.00035 = 0.00497$; $\therefore$ required dissociation constant $= [H^.] [OH'] [\text{base kations}]/[\text{undissociated base}] [H^.] = 1.3 \times 10^{-14} \times 0.00469/0.00497 \times 0.0000225 = 5.6 \times 10^{-10}.$

7. The K salt of a very weak acid saponified a Me acetate solution 3.17 times as fast when the salt concentration was $0.1N (= c_1)$ as when it was $0.01N (= c_2)$. If $Kw = 0.6 \times 10^{-14}$, calculate the dissociation constant K of the acid.

Since the Me acetate concentration is the same in each experiment, (i) $[OH']_1 = 3 \cdot 17[OH']_2$, and $K = [H'][A']/[HA] = 0 \cdot 6 \times 10^{-14}$ $[A']/[HA][OH']$ (ii). Now, since $KA + HOH = KOH + HA$, then, KA and KOH being completely dissociated and HA non-dissociated, $[K'] = [OH'] + [A']$, and (iii) $0 \cdot 1 = [A']_1 + [OH']_1$, (iv) $0 \cdot 01 = [A']_2 + [OH']_2 = [A']_2 + [OH']_1/3 \cdot 17$. We now have 3 equations, (ii), (iii), and (iv), with 5 unknowns. Two further equations are necessary in order to solve for K. From the above equation $[OH'] = [A']$ and from (ii), $[HA] = [OH'] = 0 \cdot 6 \times 10^{-14}[A']/$ $K[OH']$, whence (v) $[A']_1 = K[OH']_1{}^2/0 \cdot 6 \times 10^{-14}$ and (vi) $[A']_2 =$ $K[OH']_1{}^2/[(3 \cdot 17)^2 \times 0 \cdot 6 \times 10^{-14}]$. Divide (v) by (vi): $[A']_1{}^2/[A_2']^2$ $= (3 \cdot 17)^2$, and substitute in (iv): $0 \cdot 01 = [A']_1/(3 \cdot 17)^2 + [OH']_1/$ $3 \cdot 17$ (vii). Combine (vii) with (iii): $[A']_1/3 \cdot 17 - [A']_1/(3 \cdot 17)^2 =$ $0 \cdot 1/3 \cdot 17 - 0 \cdot 01$ or $[A']_1 = 0 \cdot 09977$. Also $[OH']_1 = 0 \cdot 1 - [A']_1$ $= 0 \cdot 00023$. From (v), $K = 0 \cdot 6 \times 10^{-14} \times 0 \cdot 09977/(0 \cdot 00023)^2 =$ *1·13 × 10⁻⁸*.

8. At 25° 1 l. of water dissolves 0·014 g. of calcspar (= 0·00014 mol). If the second dissociation constant of H_2CO_3 is $1 \cdot 3 \times 10^{-11}$ and $K_w = 1 \cdot 1 \times 10^{-14}$, calculate the degree of hydrolysis: $CaCO_3 +$ $H_2O = \frac{1}{2}Ca(HCO_3)_2 + \frac{1}{2}Ca(OH)_2$.

Since $[HCO_3'] = [OH']$, $1 \cdot 3 \times 10^{-11} = [H'][CO_3'']/[HCO_3'] =$ $1 \cdot 1 \times 10^{-14}[CO_3'']/[HCO_3']^2$. But $[CO_3''] = 0 \cdot 00014 - [HCO_3']$ mols; $\therefore [HCO_3'] = 0 \cdot 000122$, and the percentage hydrolysis is $0 \cdot 000122 \times 100/0 \cdot 00014 = $ *87 per cent.*

9. The mol. conductivity of $PhNH_2$, HCl at 25° is 113·7 ohm⁻¹ at a dilution of 128 l./mol. In the presence of excess of aniline the conductivity is 98·1 ohm⁻¹. If μ_∞ for HCl is 383, calculate the degree of hydrolysis of the salt, the hydrolysis constant, and the dissociation constant of aniline as a base, given $Kw = 1 \cdot 2 \times 10^{-14}$. What is the degree of hydrolysis of the salt in $0 \cdot 005N$ solution?

If μ = observed molecular conductivity of solution, and if $\mu_v =$ molecular conductivity of the non-hydrolysed salt and μ_{HCl} that of HCl, then, x being the degree of hydrolysis, $\mu = (1 - x)\mu_v +$ $x\mu_{HCl}$ or $x = (\mu - \mu_v)/(\mu_{HCl} - \mu_v)$. Approximately, $\mu_{HCl} = \mu_\infty =$ 383 at 25°. By adding excess of free aniline (which is practically a non-conductor) the hydrolysis is depressed, and the molecular conductivity measured under these conditions is then that of the un-hydrolysed salt. Hence $x = (113 \cdot 7 - 98 \cdot 1)/(383 - 98 \cdot 1) = $ *0·0545*. Also $K_h = x^2c/(1 - x) = (0 \cdot 0545)^2/0 \cdot 9455 \times 128 = $ *2·454 × 10⁻⁵* and $K_b = 1 \cdot 2 \times 10^{-14}/2 \cdot 454 \times 10^{-5} = $ *4·89 × 10⁻¹⁰*. Further, if y = degree of hydrolysis in $0 \cdot 005N$ solution, $2 \cdot 454 \times 10^{-5} = 0 \cdot 005y^2/$ $(1 - y)$, or $y = $ *0·068*.

10. The following figures were obtained for the inversion of cane sugar in presence of $0 \cdot 5N$ Al(NO₃)₃ at 80°:

t (min.)	0	45·7	62·1	76·8	∞
$a°$ ..	10·50	3·15	1·47	0·33	

where a is the polarimetric rotation. The inversion constant in

presence of $0.001N$ HNO_3 is 0.00225. Calculate the degree of hydrolysis of $Al(NO_3)_3$ at $80°$.

The inversion of cane sugar in presence of an acid (catalyst) is a unimolecular reaction. If A is the rotation of the solution at $t = \infty$, a_0 at $t = 0$, and a at t, then $\log(a_0 - A) - \log(a - A) = kt$ (see p. 76), where k is a constant roughly proportional to the H-ion concentration of the solution. By taking the above readings in pairs, three values for k are obtained, 0.0075, 0.0077, and 0.0078, the mean being 0.0077. The constant for $0.2N$ HNO_3 (completely dissociated) would have been $0.00225 \times 500 = 1.125$. Hence fraction of total NO_3 in solution existing as free acid $= 0.0077/1.125 = 0.007$, and the degree of hydrolysis is *0.7 per cent.*

11. The solubility of $FeCO_3$ in water containing 0.2960 mol of CO_2 per l. is 0.00303 mol/l. at $30°$. Assuming the degree of dissociation of the $Fe(HCO_3)_2$, in which form the iron exists in the solution, to be 0.902, K_1 for $H_2CO_3 = 3.75 \times 10^{-7}$ and $K_2 = 4.91 \times 10^{-11}$, show that the solubility of $FeCO_3$ in pure water would be about 6×10^{-6} mol/l. were it not hydrolytically dissociated.

The following relations hold in the solution: (i) $[H^{\cdot}]\,[HCO_3{}'] = K_1[H_2CO_3]$; (ii) $[H^{\cdot}]\,[CO_3{}''] = K_2[HCO_3{}']$; (iii) $[Fe^{\cdot\cdot}]\,[CO_3{}''] = K_3$; (iv) $[HCO_3{}'] = 2[Fe^{\cdot\cdot}]$; and (v), $[Fe^{\cdot\cdot}] = x[Fe(HCO_3)_2]$, where x is the degree of dissociation of $Fe(HCO_3)_2$. Divide (i) by (ii): $[HCO_3{}']^2/[CO_3{}''] = K_1[H_2CO_3]/K_2$, and substitute in (iii): $[HCO_3{}']^2[Fe^{\cdot\cdot}] = K_1K_3[H_2CO_3]/K_2$. Eliminate $[HCO_3{}']$ by means of (iv): $[Fe^{\cdot\cdot}]/[H_2CO_3]^{\frac{1}{3}} = (K_1K_3/4K_2)^{\frac{1}{3}} = K$ or $x[Fe(HCO_3)_2]/[H_2CO_3]^{\frac{1}{3}} = K$. Substitute the values given, $K = 0.902 \times 0.00303/(0.2960)^{\frac{1}{3}} = 0.00410$. Hence $K_3 = [Fe^{\cdot\cdot}]\,[CO_3{}''] = 4K^3K_2/K_1 = 4(0.00410)^3 (4.91 \times 10^{-11})/3.75 \times 10^{-7} = 36.1 \times 10^{-12}$. Hence the required solubility $= [Fe^{\cdot\cdot}] = K_3^{\frac{1}{2}} = 6 \times 10^{-6}$ *mol/l.*

EXERCISES.—XXVII

1. The specific conductivity of a 1 per cent solution of butyric acid $(K = 1.52 \times 10^{-5}$ at $18°)$ is 4.55×10^{-4} ohm^{-1}. If the density of the solution is 0.9994, calculate Λ_∞.

2. Calculate the degree of dissociation of HCN at a dilution of 20 l. per mol if the dissociation constant is 7.2×10^{-10} at $25°$.

3. The dissociation constant of butyric acid is 1.5×10^{-5} at $25°$. What is the degree of dissociation for an $N/10$ solution? At what concentration will the H$^{\cdot}$ ion concentration be 2×10^{-3}?

4. The specific conductivity of acetic acid solution containing 0.167 g. equiv./l. is 5.84×10^{-4} ohm^{-1} at $18°$. If $\Lambda_\infty = 350$ ohm^{-1}, calculate the H-ion concentration of the solution and the dissociation constant of the acid. At what concentration is acetic acid 5 per cent dissociated?

5. The first dissociation constant of carbonic acid is 3×10^{-7} at $18°$. Calculate the degree of the dissociation $H_2CO_3 \rightleftharpoons HCO_3{}' + H^{\cdot}$ for a dilution of 20 l./mol. If $_\infty l_{H^{\cdot}} = 315$ and $_\infty l_{HCO_3'} = 40.5$, calculate the specific conductivity of the solution.

6. The equivalent conductivity, Λ, of potassium acetate solution containing $0 \cdot 001$ mol/l. is $98 \cdot 3$ at $18°$. What concentration of acetic acid ($K = 1 \cdot 8 \times 10^{-5}$ at $18°$) can be mixed with the solution without changing the degree of dissociation of the salt? $\infty l_{K^{\cdot}} = 64 \cdot 6$; $\infty l_{Ac'} = 35$.

7. What is the H-ion concentration in 1 l. of solution containing 1 mol of butyric acid ($K = 1 \cdot 5 \times 10^{-5}$) and 1 mol of chloracetic acid ($K = 1 \cdot 55 \times 10^{-3}$)?

8. The dissociation of o-phthalic acid (regarded as monobasic) is $0 \cdot 0012$; its solubility at $17°$ is $0 \cdot 06$ g. equiv./l. Calculate [H$^{\cdot}$] in a solution of NaOH ($0 \cdot 4$ g./l.) in equilibrium with the solid acid. (The Na salt may be regarded as completely dissociated.)

9. What volumes and concentrations would it be necessary to mix in order to prepare 1 l. of mixed acetic and propionic acids ($K = 1 \cdot 9 \times 10^{-5}$ and $1 \cdot 4 \times 10^{-5}$ at $25°$, respectively) containing $0 \cdot 5$ mol of each acid without changing the degree of dissociation of the separate acids?

10. The dissociation constant of HCN is $7 \cdot 2 \times 10^{-10}$ at $25°$. How many g. of KCN (completely dissociated in solution) must be added to 1000 l. of $0 \cdot 05N$ HCN in order to yield a solution having [H$^{\cdot}$] $= 10^{-6}$?

11. The dissociation constant of acetic acid is $1 \cdot 8 \times 10^{-5}$ at $18°$. 8 g. of anhydrous Na acetate are added to 1 l. of N acid. Assuming the Na salt to be completely dissociated, calculate the H^{-} ion concentration of the solution.

12. What concentration of acetic acid ($K = 1 \cdot 8 \times 10^{-5}$) may be present in $0 \cdot 05N$ formic acid ($K = 2 \cdot 14 \times 10^{-4}$) so that the mixed solution has the same H-ion concentration as the original formic acid solution?

13. 4 g. of acetic acid ($K = 1 \cdot 9 \times 10^{-5}$ at $25°$) are added to 1 l. of $0 \cdot 5N$ glycollic acid ($K = 1 \cdot 5 \times 10^{-4}$). Calculate for each acid the ratio of its degree of dissociation before mixing to that after mixing, it being assumed that no volume change occurs.

14. 3 g. of chloracetic acid ($K = 1 \cdot 55 \times 10^{-3}$ at $25°$) are added to 1 l. of N acetic acid ($K = 1 \cdot 9 \times 10^{-5}$). Calculate the ratio of the degree of dissociation after mixing to that before mixing, for each acid.

15. If in Exercise 9 it had been required to depress the dissociation of the acetic acid by 50 per cent, what volumes and concentrations would have been required?

16. Solutions of H.COONH$_4$ in anhydrous H.COOH ($c =$ mol/l.) have the following specific conductivities, $\varkappa$, at $25°$:

| $c =$ | $0 \cdot 01162$ | $0 \cdot 04394$ | $0 \cdot 06821$ | $0 \cdot 1070$ | $0 \cdot 2711$ | $0 \cdot 4643$ |
| $\varkappa =$ | $0 \cdot 000866$ | $0 \cdot 003065$ | $0 \cdot 004581$ | $0 \cdot 006988$ | $0 \cdot 01609$ | $0 \cdot 02519$ |

For formic acid $\varkappa = 6 \cdot 35 \times 10^{-5}$ ohm^{-1} at $25°$. Show that Ostwald's dilution law is obeyed. What is the ionization constant? Use graphical methods.

17. A $0 \cdot 1N$ phenol solution has a molecular conductivity, μ, of

0·0132 at 18°, whilst $\mu_\infty = 322$. Assuming the measurements to have been carried out in air, under which condition the solution absorbs 125×10^{-7} mol/l. of CO_2, calculate the true degree of dissociation of the phenol. The first ionization constant of H_2CO_3 is $3·04 \times 10^{-7}$.

18. The mol. conductivities of aqueous CO_2 solutions at 18° are:

v (l./mol) ..	27·5	55·0	82·5	110·0	∞
μ	0·972	1·368	1·679	1·930	336

The absorption coefficient of CO_2 in water is $\beta = 1·7326 - 0·066724t + 0·0012394t^2$. If the partial pressure of CO_2 in the atm. is 0·0003 atm., calculate the specific conductivity of water which has been in contact with air at 18°.

19. The degrees of dissociation of NaCl (x_1) and HCl (x_2) solutions at 25° are ($c = $ mol/l.):

c ..	0·2	·1	·05	·02	·01	·005	·002	·001
x_1 ..	0·801	·840	·8755	·9125	·935	·9525	·9685	·977
x_2 ..	—	·921	·940	·959	·971	·980	·987	·991

Calculate the specific conductivity of a solution containing in 1 l. 0·004997 mol of NaCl ($\Lambda_\infty = 127$) and 0·001 mol of HCl($\Lambda_\infty = 424$), using the Arrhenius rule.

20. Assuming data in Exercise 19, calculate the specific conductivity of a solution containing 0·005 mol of NaCl and 0·0125 mol of HCl in a litre.

21. The ionization constant of Li formate in anhydrous formic acid is 0·557 and that of K formate 1·090. Calculate the specific conductivity of a solution of these formates in formic acid, the concentration of the Li salt being 0·1618 mol/l. and that of the K salt 0·1415 mol/l. ($\Lambda_\infty = 68·92$ for K salt and 64·72 for Li salt; see Example 4.)

22. Using graphical methods (p. 72), show from the following dissociation constants that the heat of dissociation per mol of NH_4OH is 11,000 cal. (evolved) at 200° C.

t (°C.) ..	75·2	100	124·8	156	218	306
$K \times 10^6$ ..	16·4	13·5	10·4	6·28	1·80	0·093

23. Solutions containing 1 mol each of NH_4OH (K = 0·000023), methylamine $CH_3.NH_3.OH$ (K = 0·00050), and HCl are mixed. What amount of acid is combined with the NH_4OH?

24. Solutions containing 0·6 mol each of CCl_3COOH (K = 1·21), HCOOH (K = 0·000214), and KOH are mixed. How many mols of base are combined with H.COOH?

25. Calculate the heat of dissociation of KI in EtOH at 12·5° at a dilution of 100 (l./mol) if $\Lambda = 33·54$ and $\Lambda_\infty = 52$ ohms^{-1} at 25°, and $\Lambda = 21·59$ and $\Lambda_\infty = 32$ ohms^{-1} at 0°.

26. The degree of dissociation of 0·025N NH_4OH is 0·0269 at 25°. Calculate the value on addition of 0·00125 mol of Am acetate

per 1. Calculate also the value on addition of 0·05 mol/l. of this salt. The velocity constant for the hydrolysis of Et acetate by $N/40$ KOH was found in a certain experiment to be 6·41 arbitrary units. If the KOH is 97·2 per cent dissociated at this concentration, calculate the velocity constant for the hydrolysis of this ester by $N/40$ NH₄OH and also by $N/40$ NH₄OH containing 0·0175 mol of Am acetate per 1.

27. The solubility of p-nitrobenzoic acid at 25° (K = 0·000396) is 0·00164 mol/l. of water, and 0·02451 mol/l. of a water solution containing 0·03 mol of p-toluidine. Calculate the approximate dissociation constant of the base, the acid-base complex being assumed to be 95 per cent dissociated ($Kw = 1·3 \times 10^{-14}$).

28. One 1. of a solution containing 0·0051 mol of p-nitraniline dissolves 0·000124 mol of p-nitrobenzoic acid more than 1 1. of pure water. Using data in the previous exercise, calculate the dissociation constant of the base.

29. The solubility of $AgBrO_3$ at a certain temperature is 0·00810 mol/l. Calculate the solubility after the addition of 0·0346 mol of $KBrO_3$, assuming both salts to be completely dissociated in the solution.

30. Calculate the solubility product of TlCl and its degree of dissociation in a saturated solution from the following data. The specific conductivity of a saturated solution is 1680×10^{-6} ohms⁻¹ at 20°, and the solubility at the same temperature is $1·36 \times 10^{-2}$ g. mol/l. $\Lambda_\infty = 137·3$ ohms⁻¹; Tl = 204. (Lond. B.Sc. Hons., 1925.)

31. The solubility of $Ca(OH)_2$ at 18° is 1·21 g. of CaO/l. and that of $CaSO_4$ 2·016 g./l. The respective degrees of dissociation are 0·86 and 0·55. A $0·2N$ Na_2SO_4 solution is causticized by the addition of excess of lime. Calculate the yield of NaOH.

32. The solubility of $ZnCO_3$ in water containing 0·4103 mol of CO_2 per 1. is 0·00278 mol/l. at 25°. Assuming the Zn to be present as $Zn(HCO_3)_2$, which is dissociated 89·4 per cent, and taking $K_1 = 3·50 \times 10^{-7}$ and $K_2 = 4·91 \times 10^{-11}$ for H_2CO_3, show that the solubility of $ZnCO_3$ in pure water would be $4·43 \times 10^{-6}$ mol/l. were it not hydrolytically dissociated.

33. CO_2 was passed for a short time through a suspension of $CaCO_3$. The CO_2 partial pressure of the resulting solution was 0·1422 atm.; the concentration of Ca bicarbonate was 10·66 milligram equivalents/l. Assuming the dissociation of this salt to be 0·87, that, for H_2CO_3, $K_1 = 3·04 \times 10^{-7}$ and $K_2 = 1·295 \times 10^{-11}$, and that 1 1. of water dissolves 0·9753 1. of CO_2 at 760 mm., calculate the solubility product of $CaCO_3$.

34. Calculate approximately the number of mols of MeCOOH which must be added to N Na acetate solution so that the solution will be neutral. $K_w = 1 \times 10^{-14}$; K(HAc) = $1·8 \times 10^{-5}$.

35. A $0·0119N$ solution of Na_2CO_3 is $0·00338N$ with respect to OH'. If K_w is $1·04 \times 10^{-14}$, and if Na_2CO_3 is 74 per cent dissociated into Na' and CO_3'', calculate the second dissociation constant of H_2CO_3. ($CO_3'' + H_2O = OH' + HCO_3'$.)

36. The molecular conductivity of m-toluidine hydrochloride is 116

at a dilution of 256; in presence of excess of aniline the conductivity is
97. If μ_∞ for HCl is 383 at 25°, calculate the degree of hydrolysis.

37. The hydrolysis of $N/32$ Me acetate solution at 100° by $N/500$
HCl proceeds as follows, a being the titre of 10 c.c. of the solution
at time t:

t ..	0	64	113	152	min.
a ..	1·10	4·15	6·03	7·35	$N/50$ NaOH.

If the velocity constant for the catalysis of $N/32$ Me acetate by a solu-
tion of $AlCl_3$ containing 1/32 g. mol/l. is 0·00216 at 100°, calculate
the degree of hydrolysis of the $AlCl_3$ solution, assuming the velocity
constant to be proportional to the concentration of HCl.

38. The following rotations, a, were observed for a 20 per cent
cane-sugar solution in presence of $N/30$ urea hydrochloride (tempera-
ture = 60°):

t (min.) ..	0	19·5	40·7	59·0	∞
a	10·63	5·40	1·78	−0·13	−3·55

The inversion constant for the same solution in presence of $N/30$
HCl = 0·0113. Calculate the percentage hydrolysis of the salt.

39. What weight of solid NH_4Cl must be added to a mixture of
100 c.c. of $0·5N$ NH_4OH solution and 100 c.c. of $0·5N$ $MgCl_2$ solution,
so that the precipitate will just redissolve? Assume the solution of
NH_4Cl to be unaccompanied by volume change; dissociation constant
of $NH_4OH = 1·8 \times 10^{-5}$; solubility product of $Mg(OH)_2 = 1·22 \times 10^{-11}$.
Assume all neutral salts to be completely dissociated.

40. The solubility of TlCl at 25° is 1·70 molal, the activity coefficient
of Tl· being 0·5. Calculate ΔZ for the reaction Tl· + OH′ = TlOH (s).

41. The solubility product of $AgIO_3$ at 25° is $3·3 \times 10^{-8}$. Show
that ΔZ for the reaction $AgIO_3 = Ag· + IO_3′$ is 10,260 cal. at this
temperature.

42. Show that: $s = -\dfrac{cx_1}{2x} + \sqrt{\dfrac{c^2 x_1^2}{4x^2} + \dfrac{s_0^2 x_0^2}{x^2}}$, . . . (175)

where s_0 and s are the solubilities, and x_0, x the degrees of dissociation,
of a uni-univalent electrolyte before and after the addition of a second
electrolyte with a common ion. The concentration of this electrolyte
in the mixture is c and its degree of dissociation x_1. (Assume (169).)

The solubility of α-brom-*iso*cinnamic acid (K = 0·0144) is 0·0176
mol./l. To a litre of saturated solution 0·0272 mol of oxanilic acid was
added. The degree of dissociation of the first acid was estimated to
be 0·453 and that of the added acid 0·403, in the solution. What
amount of the brom-acid is precipitated from solution?

43. Using data in the preceding exercise, calculate the solubility of
α-brom-*iso*cinnamic acid in a solution containing 0·0524 mol of
oxanilic acid per l. The degrees of dissociation of the respective acids
in the mixed solution are estimated to be 0·39 and 0·34.

44. For NEt_4I solution, $\Lambda = 111·5 - 604·5 c^{1/3}$ and for KI solution
$\Lambda = 151·2 - 399 c^{1/3}$ at 25°, where c is in g. equivalent/c.c. Calculate by

Barmwater's method the specific conductivity of a solution containing 1.854×10^{-3} g. equivalent of NEt_4I and 6.008×10^{-3} g. equivalent of KI per l.

45. The OH′ concentration of a saturated aqueous solution of Ag_2O at 25° is $1.4 \times 10^{-4}M$. Calculate ΔZ for the reaction: $Ag_2O + H_2O = 2Ag^{\cdot} + 2OH′$.

(c) ELECTROMOTIVE FORCE (E.M.F.)

(1) Thermodynamics of Cells.

If a reversible chemical process takes place in a cell, the E.M.F., E, of the latter is related to the maximum available work of the process by the equation (C. T., p. 207)

$$-\Delta Z = A = yEF, \quad . \quad . \quad . \quad . \quad (176)$$

where y Faradays are transported. Combining (176) and (133) we have

$$E = (RT/yF) \ln K(C_1^{n_1} \times C_2^{n_2} \times .../C_1'^{n_1'} \times C_2'^{n_2'} \times ...). \quad (177)$$

If Q is the heat of the reaction occurring in the cell, then (176) and (65) give

$$E = Q/yF + T . dE/dT. \quad (178)$$

The quantity $T . dE/dT$ is the *latent heat*, λ, per electrochemical equivalent.

Units.—In (177), F is in coulombs (96,500) and R in joules/1° ($= 8.3156$); E is then in volts. In (178), if E is in volts Q must be in volt-coulombs or joules (1 joule $= 0.2390$ cal.); if Q is in cal., then (178) may be written (E in volts):

$$E = Q/23,040y + T . dE/dT. \quad . \quad (178a)$$

(2) Electrode Potentials.

The E.M.F. of a cell is the potential difference (P.D.) between the terminals when no current is passing. It may be regarded as made up of separate P.D.'s, one at *each* contact of dissimilar materials in the cell. If the cell is composed of two electrodes in the same solution then the E.M.F. is the algebraic *difference* of the P.D.'s between each electrode and the solution,

$$E = E_1 - E_2, \quad . \quad . \quad . \quad . \quad (179)$$

where E_1 and E_2 are the *single electrode potentials* (S.E.P.). The sign of these is arbitrary: in the present book (as in recognized European practice) the sign of the charge on the *electrode* is taken as the sign of the S.E.P., i.e. the latter indicates by how much the potential of the electrode is greater (S.E.P. > 0) or less (S.E.P. < 0) than that of the solution. American writers (Lewis and Randall; Taylor) adopt the sign of the solution, which is an older convention.

If the two electrodes are immersed in two different solutions, there is generally a P.D. at the contact between these, and (179) is true only when this P.D., called the *diffusion potential*, E_d, is zero or negligible or has been eliminated by calculation or otherwise. The E.M.F. is now composed of the following potential differences: electrode 1/solution 1/solution 2/electrode 2.

We agree always to let E_1 represent the potential of the left-hand electrode of a cell as written, and E_2 that of the right-hand electrode; the resulting E.M.F. is then positive if the positive current flows *within* the cell from right to left.

The P.D. between an electrode and its solution is called the *absolute* S.E.P. and is generally regarded as unknown. Single potentials are usually expressed with reference to some second, standard, electrode, the potential of which is *arbitrarily* taken as zero ($E_2 = 0$) at all temperatures when comparison is made with another electrode. The most usual standard electrodes are the N-hydrogen electrode and the N-calomel electrode. In electrostatics the potential of the earth is taken as a practical zero, which is an entirely different convention. The value of E is clearly independent of whatever standard of reference is taken as zero in E_1 and E_2. By means of the dropping electrode and capillary electrometer a value $+ 0.274$ volt at $18°$ has been obtained for the potential of the Pt plate of the N-H_2 electrode with respect to the solution supposed at the potential of the earth, and this is usually referred to as the *absolute* potential of this electrode. The absolute potential of the N-calomel electrode is $+ 0.560$ volt at $18°$, the Hg being positive with respect to the solution. To convert single potentials determined with reference to the N-H_2 electrode as zero into absolute potentials, 0.274 is added to them; single potentials referred to the N-calomel electrode are converted into absolute potentials by addition of 0.560.

Potentials of Calomel Electrodes (H = 0)

	0°	18°	25°
N-cal. electrode ..	$+0.2720$	0.2830	0.2873
$0.1N$-cal. electrode ..	$+0.3208$	0.3350	0.3405

Unless otherwise stated, single potentials used in this book are referred to the N-H_2 electrode.

According to Nernst's solution pressure theory, the *absolute* single potential of an electrode at which the equilibrium $M^{y\oplus} \rightleftharpoons M + y\oplus$ exists is

$$E_1 = - RT/yF . \ln(\pi/p), \quad . \quad . \quad . \quad (180)$$

where π is the *solution pressure* of M and p is the *osmotic pressure* of the corresponding ions $M^{y\oplus}$ in the solution. If c is the concentration of these ions (in g. ions/l.) then $p = kc$, where k is a constant, and

$$E_1 = - RT/yF.\ln(\pi/k) + RT/yF.\ln c = E_0 + RT/yF.\ln c, (181)$$

where E_0 is a constant, the *normal* or *standard electrode potential*, or *electro-affinity*, for a given metal or other electrode material at a given temperature. An application of (177) to the ionic equilibrium shows that $E_0 = - RT/yF . \ln K$, i.e. E_0 is a measure of the standard affinity of the electrode process.[*] Equation (181) shows that E_0 is the potential of an electrode when the solution contains 1 g. ion per litre. The concentration c is more accurately replaced in (181) by the ion activity.

Units.—As before, with R in joules and F in coulombs, E_1 is expressed in volts. If in (181) the natural logarithms are converted into common logarithms, then, approximately:

$$E_1 = E_0 + 0.0002\,T/y . \log c. \quad . \quad . \quad (181a)$$

If this is written $E_1 = E_0 + \xi/y . \log c$ we have:

T =	288	291	293	298	303
ξ =	0.05715	0.05774	0.05814	0.05913	0.06011

Values of E_0 will be found on p. 142. It must be remembered that the diffusion potentials between· the acid of the N-H_2

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[*] It should be noted that E_0 is a function of T. Strictly speaking, therefore, equation (181) can only be applied at those temperatures for which E_0 is known. Actually, the variation of E_0 with T is slight and in practice is neglected. If dE_1/dT is found, an application of (178) to a single electrode gives a value of the *heat of ionization* (*C. T.*, § 111).

electrode and salt solutions are considerable. These are not included in the tabulated values.

(3) Concentration Cells.

Concentration cells of the first class are represented by: $M/M^\cdot(c_1)//M^\cdot(c_2)/M$. Since E_0 is the same for each electrode, then from (181) $(c_1 > c_2)$:

$$E = RT/yF \cdot \ln c_1/c_2, \quad . \quad . \quad . \quad (182)$$

Equation (182) does not allow for diffusion potential, which, however, may often be eliminated by the interposition of a suitable solution at the liquid junction. The cell is then usually written with a double solidus at the eliminated junction.

Concentration cells of the second class are represented by: M amalgam $(c_1) / M^{y\oplus}(c')/M$ amalgam (c_2). The reaction $M^{y\oplus} \rightleftharpoons M + y \oplus$ occurs *at* each electrode. *Within* the electrode the reaction $M_m \rightleftharpoons mM$ occurs, the mol. wt. of M in the amalgam being m times the at. wt. Then * $[M]^m = k[M_m]$, and the application of (180) to each electrode gives

$$E_1 = - RT/yF \cdot \ln k_1 \sqrt[m]{kc_1}/K'c' \ (\pi = k_1[M]_1; \ p = K'c');$$

$$\therefore \ E = E_1 - E_2 = RT/myF \cdot \ln c_2/c_1 . \quad . \quad (183)$$

Usually $m = 1$.

(4) Diffusion Potential.

If two solutions at a liquid junction in a cell contain the *same completely ionized uni-univalent electrolyte* at concentrations c_1 and c_2 $(c_1 > c_2)$ and if l_k, l_a are the mobilities of the kation and anion, respectively, then the P.D. between them is:

$$E_d = (l_a - l_k)/(l_a + l_k) \cdot RT/F \cdot \ln c_1/c_2. \quad (184)$$

If the two solutions contain *different completely ionized uni-univalent electrolytes* at the *same ionic concentration*, then

$$E_d = RT/F \cdot \ln(l_k + l_a')/(l_k' + l_a), \quad . \quad (185)$$

where l_a, l_k refer to the ions of one electrolyte and l_a', l_k' refer to those of the other. If the electrolytes are *bi-bivalent* the right-

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* For convenience in printing [ ] has been used to represent concentration generally in this chapter.

hand side of (185) must be divided by two. If the two solutions in the former case have a *common ion*, then according to Lewis and Sargent

$$E_d = RT/F \cdot \ln \Lambda_1/\Lambda_2, \quad . \quad . \quad . \quad (186)$$

where Λ = equivalent conductivity.

Sign of Diffusion Potential.—In (184) $\ln c_1/c_2$ is always positive, and the value of E_d, which is the drop of potential from strong to weak solution, gives the sign of the charge on the concentrated solution. This is positive or negative according as the speed of the anion or kation, respectively, is the greater. Since diffusion of *both* ions will always occur from the strong to the weak solution, the latter assumes the sign of the charge on the more mobile ion. The question whether E_d should be added to or subtracted from E to find $E_1 - E_2$ is best decided as in the following examples.

(i) The E.M.F. of the cell Hg/HgCl N KCl/N NaOH Cu$_2$O/Cu is $+$ 0·610 volt at 16°. The positive current *in* the cell, therefore, flows from Cu to Hg. The numerical value of the diffusion potential is 0·02 volt. Now OH′ is the fastest ion at the junction, and hence the diffusion process results in negative electricity being carried from NaOH to KCl. In other words, positive current is carried from KCl to NaOH i.e. in the *opposite direction* to the main current in the cell (the current produced by the chemical reaction taking place in the cell). Since, therefore, the junction potential is *hindering* the main current of the cell, the measured potential (0·610 volt) will be smaller than the true potential by E_d, i.e. by 0·02 volt, and $E_1 - E_2$ for the above cell is 0·610 $+$ 0·02 = 0·630 volt. Since the potential of the N-calomel electrode is $+$ 0·282 volt, the potential, E_2, of the electrode Cu/Cu$_2$O N NaOH is given by 0·630 = 0·282 $- E_2$ or $E_2 = -$ 0·348 volt.

(ii) The E.M.F. of the cell Ag/0·01N AgNO$_3$/0·001NAgNO$_3$/ Ag is $+$ 0·058 volt. The numerical value of the diffusion potential is 0·0032 volt. The faster ion at the junction is NO$_3$′, and since salt will diffuse from the concentrated to the dilute solution negative electricity will be carried through the cell in this direction. The main (positive) current of the cell passes from the dilute to the concentrated solution. Hence the diffusion potential *assists* the main current. The measured E.M.F., therefore, is too large by an amount E_d and $E_1 - E_2$ is 0·058 $-$ 0·003 = 0·055 volt.

The sign of E_d is independent of all conventions concerning the sign of the electrode potential; it depends solely on the direction at the junction of the current produced by diffusion.

Two junctions which lie between similar pairs of solutions with the same *ratio* of concentrations have the same E_d; e.g. the P.D. between NHCl and NKCl is the same as that between $0 \cdot 1N$ HCl and $0 \cdot 1N$ KCl (*Nernst's principle of superposition*).

(5) Gas Electrodes.

The potentials of gas electrodes may be found from (177).

In the case of the H_2 *electrode* $H \cdot \rightleftharpoons \frac{1}{2}H_2 + \oplus$, and from (177) $E_{H_2} = (RT/F) \ln K (p_{H\cdot}/p_{H_2}^{\frac{1}{2}})$ where $p_{H\cdot}$ represents the osmotic pressure of $H \cdot$ in the solution and p_{H_2} is the pressure of H_2 gas. Since $p_{H\cdot} = k[H \cdot]$,

$$E_{H_2} = RT/F \cdot \ln k'[H \cdot]/p_{H_2}^{\frac{1}{2}} = E_0 + RT/F \cdot \ln [H \cdot]/p_{H_2}^{\frac{1}{2}}. \quad (187)$$

In this particular case E_0 is arbitrarily taken as zero ([$H \cdot$] = 1; $p = 1$ atm.; *practical* scale).

For the O_2 *electrode* $O_2 + 2H_2O \rightleftharpoons 4OH' + 4 \oplus$, and from (177) $E_{O_2} = (RT/4F) \cdot \ln K p_{O_2}/p_{OH'}^4$; since $p_{OH'} = k[OH']$,

$$E_{O_2} = RT/4F \cdot \ln k' p_{O_2}/[OH']^4$$
$$= E_0 + RT/F \cdot \ln p_{O_2}^{\frac{1}{4}}/[OH']. \quad . \quad . \quad (188)$$

For the Cl_2 *electrode* $Cl_2 \rightleftharpoons 2Cl' + 2 \oplus$, and as before

$$E_{Cl_2} = E_0 - RT/F \cdot \ln [Cl']/p_{Cl_2}^{\frac{1}{2}}. \quad . \quad (189)$$

(6) Oxidation-reduction Electrodes.

The potentials of electrodes at which oxidation or reduction reactions occur may be determined with the aid of (177). Two cases arise according as the reaction is (*a*) non-ionic or (*b*) ionic.

(*a*) $C_2H_4 + H_2 = C_2H_6$. A Pt strip bathed in $C_2H_6 + C_2H_4$ and immersed in a solution of $H \cdot$ ions will behave as a hydrogen electrode in which $p_{H_2} = \text{constant} \cdot p_{C_2H_6}/p_{C_2H_4}$. Hence from (177):

$$E_{H_2} = RT/F \cdot \ln \text{const.} [H \cdot] \cdot p^{\frac{1}{2}}_{C_2H_4}/p^{\frac{1}{2}}_{C_2H_6}$$
$$= E_0 + RT/F \cdot \ln [H \cdot] p^{\frac{1}{2}}_{C_2H_4}/p^{\frac{1}{2}}_{C_2H_6}.$$

(*b*) $FeCl_3 + \frac{1}{2}H_2 = FeCl_2 + HCl$. This may be written $Fe^{\cdots} + \frac{1}{2}H_2 = Fe^{\cdot\cdot} + H^{\cdot}$, and if this is divided into two parts: $Fe^{\cdots} \rightarrow Fe^{\cdot\cdot} + \oplus$; $\frac{1}{2}H_2 + \oplus = H^{\cdot}$, y is seen to be 1. Also $p_{H_2} = k'[H_2]_{sol.} = k''[H^{\cdot}]$. Hence, from (177):

$$E = RT/F . \ln K'[Fe^{\cdots}]p_{H_2}^{\frac{1}{2}}/[Fe^{\cdot\cdot}][H^{\cdot}]$$

A more complicated example is afforded by the permanganate-manganous electrode: $MnO_4' + 3H^{\cdot} + 5/2 . H_2 = Mn^{\cdot\cdot} + 4H_2O$. The main reaction is $MnO_4' \rightarrow Mn^{\cdot\cdot} + 4O'' + 5\oplus$. Hence $y = 5$, and from (177):

$$E =$$

But $\qquad \cdot] = k'$, or $\qquad ^{\prime} = k'[H^{\cdot}]^5$. Hence

$$E = E_0 + RT/5F . \ln[MnO_4'][H^{\cdot}]^8/[Mn^{\cdot\cdot}].$$

EXAMPLES.—1. The following example illustrates the difference between European and American nomenclature.

American	*European*
The E.M.F. of the cell $(-)$Ag, AgCl/KCl aq./HgCl, Hg$(+)$ is $+0\cdot0455$ volt at $25°$. Calculate ΔF for the reaction Ag (s) + HgCl (s) = AgCl (s) + Hg (l).	The E.M.F. of the cell $(+)$Hg, HgCl/KCl aq./AgCl, Ag$(-)$ is $+0\cdot0455$ volt at $25°$. Calculate ΔZ for the reaction Ag (s) + HgCl (s) = AgCl (s) + Hg (l).
According to American convention the given E.M.F. represents the tendency of negative current to pass *spontaneously* through the cell (as written) from *right* to *left*. Hence, for the above reaction, $E = +0\cdot0455$ volt and $\Delta F = -yEF = -23,040 \times 0\cdot0455$ cal. $= -1048$ cal.	According to convention (p.113) the given E.M.F. represents the tendency of positive current to pass *spontaneously* through the cell (as written) from *right* to *left*. Hence, for the above reaction, $E = +0\cdot0455$ volt and $\Delta Z = -yEF = -23,040 \times 0\cdot0455$ cal. $= -1048$ cal.

2. The E.M.F. of the cell $Hg/Hg_2SO_4/Na_2SO_4$ sol./$PbSO_4/Pb_2Hg$, Hg is $E = 0\cdot96463 + 0\cdot000174(t - 25) + 0\cdot0_638(t - 25)^2$. If 585 cal. are evolved by the removal of 1 g. atom of Pb from a heterogeneous Pb amalgam containing Pb_2Hg as the solid phase, calculate the heat of the reaction occurring in the cell at $18°$.

Since $\frac{1}{2}Pb_2 \rightarrow Pb^{\cdot\cdot} - 2\oplus$ and $Hg_2^{\cdot\cdot} \rightarrow 2Hg + 2\oplus$ the passage of $2F$ causes the following reaction to occur: $\frac{1}{2}Pb_2Hg + Hg_2SO_4 = PbSO_4 + 2\frac{1}{2}Hg$. At $18°$, $E = 0\cdot96343$ volt and $dE/dT = 0\cdot000169$

volt/1°; hence from (178): $Q = 2F(0.96343 - 291 \times 0.000169)$
$0.2387 = 42,139$ cal. Deduct 585 from this; the heat of the reaction
$Pb + Hg_2SO_4 = PbSO_4 + 2Hg$ occurring in the cell is then *41,554 cal.*

3. $AlCl_3$ is assumed to hydrolyse according to the equation $AlCl_3 + H_2O = AlCl_2(OH) + HCl$. The E.M.F. of the cell N-cal. electrode $/NH_4NO_3/AlCl_3(v = 64) /Pt(H_2)$ is 0.4655 volt. The absolute potential of the N-calomel electrode is $+ 0.56$ volt and that of the N-hydrogen electrode is $+ 0.277$ volt. Calculate the percentage hydrolysis of $AlCl_3$ if the dissociation of the HCl produced is 91.2 per cent.

The reaction is (x = degree of hydrolysis; v = dilution):

$$AlCl_3 + H_2O = AlCl_2(OH) + HCl[\rightleftharpoons H^. + Cl'].$$
$$(1-x)/v \qquad\qquad x/v \qquad x/v \quad \alpha x/v \quad \alpha x/v$$
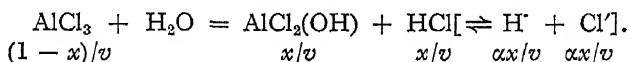
Now $E = E_1 - E_2 = E_{cal.} - (E_0 + 0.059 \log[H^.]) = 0.4655$ volt.
Hence $E_0 + 0.059 \log[H^.] = 0.56 - 0.4655 = 0.0945$ volt; and since
$E_0 = + 0.277$ volt, $[H^.] = 0.807 \times 10^{-3}$. The degree of dissociation
of the HCl is 0.912; hence the *total* HCl concentration $= 0.807 \times 10^{-3}/0.912 = 0.885 \times 10^{-3} = x/v$, so that $x = 0.885 \times 10^{-3} \times 64$
$= $ *5.66 per cent.*

4. The E.M.F. at 18° of the cell $Pt/Hg(ClO_4)_2, Hg_2(ClO_4)_2/$
$0.1N$ KNO_3/N-cal. electrode, is 0.5540 volt when the concentration
of the mercuric salt is 0.0160 mol/l. and that of the mercurous salt
0.0770 mol/l. The degree of dissociation of each salt is about 0.73
and the degree of hydrolysis 3 per cent. If the absolute potential of
the N-cal. electrode is $+ 0.560$ volt at 18°, calculate the absolute normal
oxidation-reduction potential of Hg.

The cell reaction is $2Hg^. = Hg_2^{..} + 2 \oplus$. Hence the electrode
potential, E, of the perchlorate half of the cell is given by $E = E_0 + 0.029 \log[Hg^.]^2/[Hg_2^{..}]$, where E_0 is the normal oxidation potential.
If x_1 and x_2 are the degrees of dissociation of the mercuric and mer-
curous perchlorates, respectively, then $E = E_0 + 0.029 \log[Hg(ClO_4)_2]^2$
$/[Hg_2(ClO_4)_2] + 0.029 \log x_1^2/x_2$. Since $x_1 = x_2 = 0.73$ and the degree
of hydrolysis $= 0.03$, then the last term is $0.029 \log(0.73 \times 0.97)$
$= - 0.0044$ volt. Hence $0.5540 = E_0 + 0.029 \log(0.016)^2/(0.077) -$
0.0044 or $E_0 = 0.5540 + 0.0719 + 0.0044 = 0.6303$ volt. The
absolute value of E_0 is thus $0.6303 + 0.56 = $ *1.1903 volt.*

5. The E.M.F. of the cell N-cal. electrode$/KCl(0.1M)/KCl$ $(0.01M)/$
KOH $(0.01M)/H_2$ is 0.9761 volt at 25°. The equivalent conductivities
are: $0.01M$ KOH, 256; $0.01M$ KCl, 141.4; $0.1M$ KCl, 129.0; and
the average transport number of $K^.$ between $0.1M$ and $0.01M$ KCl
is 0.494. The E.M.F. of the cell N-cal. electrode$/KCl$ $(0.1M)/KCl$
$(0.01M)/HCl$ $(0.01M)/H_2$ is 0.4261 volt at the same temperature.
Λ for $0.01M$ HCl is 411.6, and the degree of dissociation is 0.92. The
same dissociation holds for $0.01M$ KOH. Calculate K_w, the ionization
constant for water.

At the junction KCl/KOH of the first cell the OH' is the faster ion

and E_d' must be added to the observed E. From (186), $E_d' = 0.059$ $\log 141.4/256 = 0.01524$ volt. At the KCl junction Cl′ is the more rapid ion and E_d'' must be subtracted from the observed E. Use (167) and (184); $(0.506 - 0.494) \times 0.059 \times \log(0.1 \times 129/0.01 \times 141.4) = 0.0007$. Hence the corrected E.M.F. is $0.9761 - 0.0007 + 0.0152 = 0.9906$ volt. Similarly for the second cell $E = 0.3980$ volt. The E.M.F. of the cell $H_2/HCl(0.01M)//KOH \ (0.01M)/H_2$ is thus $0.9906 - 0.3980$ $= 0.5926$ volt. But $0.5926 = 0.059 \log[H\cdot]_1/[H\cdot]_2 = 0.059 \log(0.92 \times$ $: 0.059 \log(0.92 \times 0.01)^2/K_w$ or $K_w = 0.79 \times 10^{-14}$.

6. The E.M.F. of the cell $Hg/Hg_2Cl_2 \ 0.1N \ KCl/0.1N \ KOH +$ Cu_2O/Cu is 0.605 volt at 17°, at which temperature K_w is 0.56×10^{-14}; the potential of the $0.1N$-calomel electrode is 0.335 volt referred to the N-H_2 electrode, and that of the electrode $Pt(H_2)/0.1N \ KOH$, $- 0.758$ volt. If the liquid junction potential $0.1N \ KCl/0.1N \ KOH$ is 0.015 volt, calculate the solubility product of CuOH, $[Cu\cdot][OH']$ $= k$. $(E_{0 \ Cu\cdot \longrightarrow \ Cu} = 0.454 \ volt.)$
   The E.M.F. of the calomel-Cu cell is $+ 0.605$ volt $= E_1 - E_2$, where E_1 refers to the $0.1N$-calomel electrode and E_2 to the $Cu - Cu_2O$ electrode. Since E is positive the Hg is positive and the Cu negative. But at the junction KOH is positive and KCl negative, i.e. a P.D. of 0.015 volt acts in the opposite direction to the main current of the cell. Hence the observed E.M.F. is too small by 0.015 volt and $0.605 + 0.015 = 0.335 - E_2$, whence $E_2 = - 0.285$ volt. We can now build up a cell in which the reaction $H_2 + Cu_2O = 2Cu + H_2O$ occurs; it is $Pt(H_2)/0.1N \ KOH + Cu_2O/Cu$ and its E.M.F. is $- 0.758 - (- 0.285) = - 0.473$ volt. The electrode reactions in this cell are $H\cdot \rightleftharpoons \frac{1}{2}H_2 + \oplus$ and $Cu\cdot \rightleftharpoons Cu + \oplus$; hence its E.M.F. is $E' = (E_0 + 0.058 \log[H\cdot])_H - (E_0 + 0.058 \log[Cu\cdot])_{Cu} = 0.058 \log[H\cdot]/$ $[Cu\cdot] - (E_0)_{Cu} = 0.058 \ \log K_w/k - (E_0)_{Cu} = 0.058 \ \log 0.56 \times 10^{-14}/$ $k - 0.454$. But $E' = - 0.473$. Hence $k = 1.2 \times 10^{-14}$.

7. Find a general expression for the electrode potential $N_2 \longrightarrow NH_3$ in alkaline solution from a consideration of the hypothetical cell $NH_3(g)N_2(g)/OH'/Pt(H_2; \ 1 \ atm.)$, in which the reaction $\frac{3}{2}H_2 + \frac{1}{2}N_2$ $= NH_3$ is taking place. The equilibrium constant of this reaction is given by $\log p^3_{H_2}p_{N_2}/p^2_{NH_3} = - 21,980/4.576 \ T + 3.5 \log T + 0.00331T$ $/4.576 - 8.1 \times 10^{-10}T^3/4.576 + 0.440$. The electrode $Pt(H_2; \ 1 \ atm.)$ $/N \ NaOH$ has a potential of $- 0.825$ volt at 25° and for aqueous ammonia solutions p_{NH_3} (atm.) $= 0.0176[NH_3]$.
   Find also the potential of the electrode $N_2 \longrightarrow NH_4\cdot$, given that K_w $= 1.14 \times 10^{-14}$ and $k' = [NH_4\cdot][OH']/[NH_3] = 1.9 \times 10^{-5}$, both at 25°.
   First find the standard affinity of the cell reaction at 298° K.: $A = RT \ln K = 8.316 \times 298 \times 2.303 \times 3.405 = 19,430$ joules. This arbitrarily supposes the free concentrations to be unity (cf. p. 71). The electrode reactions are: $\frac{1}{2}N_2 + 3H_2O = NH_3 + 3OH' + 3 \oplus$ and $\frac{3}{2}H_2 + 3OH' = 3H_2O - 3 \oplus$. Hence $y = 3$ and the E.M.F. of the cell (all the substances still being at unit free concentration) is (equation 176) $19,430/3 \times 96,500 = 0.0671$ volt. The same result

would have been obtained had the cell reaction been assumed to be $3H_2 + N_2 = 2NH_3$. Hence, $0.0671 = E_1 - (- 0.825)$, or $E_1 = - 0.758$, the potential of the $N_2 \longrightarrow NH_3$ electrode at $25°$, and, since the free concentrations have been taken as unity throughout, this is the standard electrode potential (for $N_2 \longrightarrow NH_3$ in alkaline solution). To determine E_1 for any free concentration, E_1', equation (177) is applied to the electrode reaction, $\frac{1}{2}N_2 + 3H_2O = NH_3 + 3OH' + 3 \oplus$. Since $y = 3$, we have $E_1' = E_1 + RT/3F \cdot \ln p^{\frac{1}{2}}_{N_2}/p_{NH_3}[OH']^3 = - 0.758 + RT/6F \cdot \ln p_{N_2}/p^2_{NH_3}[OH']^6$, which, at $25°$, equals $- 0.724 + 0.00984 \log p_{N_2}/[NH_3]^2[OH']^6$. When the reaction proceeds in acid solution, $N_2 \longrightarrow NH_4^{\cdot}$, and, by substituting for $[OH']$ and $[NH_3]$ with the data given, $E_1' = - 0.725 + RT/6F \cdot \ln p_{N_2}[H^{\cdot}]^8/[NH_4^{\cdot}]^2(1.14 \times 10^{-14})^6(6 \times 10^{-10})^2 = + 0.281 + RT/6F \cdot \ln p_{N_2}[H^{\cdot}]^8/[NH_4^{\cdot}]^2$, where the standard potential, $+ 0.281$ volt, refers to $25°$.

8. The potential of the electrode $N_2 \longrightarrow NO_2'$ in alkaline solution is $E_1 = 0.41 + 0.059/6 \cdot \log[NO_2']^2/p_{N_2}[OH']^8$ at $25°$. Using the result of the previous example, demonstrate that NH_4NO_2 is unstable in solution at $25°$.

The process corresponding to E_1 is $N_2 + 8OH' = 2NO_2' + 4H_2O - 6 \oplus$ and that corresponding to the electrode $E_2(N_2 \longrightarrow NH_4^{\cdot})$, is $N_2 + 8H^{\cdot} = 2NH_4^{\cdot} + 6 \oplus$. The total reaction occurring in a combination of these electrodes is the *sum* of these partial reactions: $2N_2 + 4H_2O = 2NH_4^{\cdot} + 2NO_2'$, and the E.M.F. of a cell in which this reaction would occur is $E_1 - E_2$. Equilibrium is attained ($A = 0$ and $\therefore$ $E = 0$) when $E_1 = E_2$. Equate the expressions for E_1 and E_2, and assume we are dealing with a solution in which $[NH_4^{\cdot}] = [NO_2'] = 1$; we find $p_{N_2} = 10^{62 \cdot 4}$ atm. Obviously, when p_{N_2} exceeds this value the reaction $N_2 \longrightarrow NH_4^{\cdot} + NO_2'$ will proceed. Under ordinary conditions ($p_{N_2} = 0.8$ atm.) the reverse reaction will proceed if circumstances are favourable. Actually the dilute solution is stable at $25°$ if it is slightly alkaline.

9. The E.M.F. of the cell $Hg/HgCl$, KCl solution/AgCl, KCl solution/Ag is 0.0455 volt at $25°$ and $dE/dT = 0.000338$ volt/$1°$. Calculate the entropy change accompanying the reaction $Hg + AgCl = Ag + HgCl$.

The E.M.F. of a cell in which the given reaction occurs is $- 0.0455$ volt. The heat of this reaction is (178a): $Q = 23,040(- 0.0455 - 298 \times 0.000338) = - 3369$ cal. Also, from (176), $\Delta Z = - yEF = 1 \times 0.0455 \times 96,500 \times 0.239 = 1049$ cal. But (cf. equation 62): $- \Delta Z - Q = T\Delta S$. Hence: $- 1049 + 3369 = 298\Delta S$ or $\Delta S = 7.76$ cal./$1°$.

10. The electrolysis of potassium oxalate solution with a tin anode yields a solution containing Sn almost completely as complex anions, $Sn_x(C_2O_4)_y$. Find the values of x and y from the observed E.M.F., E, of the cell Hg/Hg_2Cl_2, saturated KCl/saturated KCl/anolyte/Sn containing such a solution as anolyte. M is the total concentration of Sn in g. atom/l.; η' is the viscosity of anolyte referred to pure water as unity and R is the resistance of an arbitrary vol. v of the solution in ohms. N is the normality of the K oxalate solution.

First Series.		Second Series.		
E	M	N	E	$\log(\eta'/\mathrm{R})$
0·7798	$1·0000 \times 10^{-2}$	2·0	0·7866	$\bar{2} + 0·9166$
·7823	·83333	2·5	·7937	1·0037
·7842	·7143	3·0	·7990	1·0794
·7859	·6250	3·5	·8002	1·1450
·7877	·5556	4·0	·8052	1·1981

In the first series of experiments the concentration of the oxalate ion was kept constant (2 normal); in the second series M was kept constant at 1×10^{-2}. Assume $\alpha = \eta\Lambda/\eta_\infty\Lambda_\infty$, where η = viscosity of solution and η_∞ = that of water.

In the anolyte solution the following reaction occurs: $Sn_x(C_2O_4)_y$ $\rightleftharpoons xSn^{..} + yC_2O_4''$. Hence: $[Sn^{..}]^x[C_2O_4'']^y = K[Sn_x(C_2O_4)_y]$ or $x \log[Sn^{..}] + y \log[C_2O_4''] = \log K + \log[Sn_x(C_2O_4)_y]$. But $E = E_{satd.\ cal.} - (E_0 + 0·029 \log_{10}[Sn^{..}])_{Sn^{..}} = k - 0·029 \log_{10}[Sn^{..}]$, where k is a constant. Now $[Sn^{..}]$ is very small; hence $[Sn_x(C_2O_4)_y] = M/x$ and, finally, $x(k - E)/0·029 + y \log[C_2O_4''] = \log K + \log M - \log x$, which, for the first series, is a linear relation between $\log M$ (ordinate) and E, the slope being $-x/·029$. On plotting these quantities the slope is found to be $-0·25/0·00747$. Hence $x = 0·25 \times 0·029/0·00747 = 0·97$ or 1, since it must be a whole number.

To find y, values of E are recorded for a constant value of M. Under these conditions the above equation becomes a linear relationship between E (abscissa) and $\log[C_2O_4'']$, the slope being $1/0·029y$ (since $x = 1$). But α, the degree of dissociation of the K oxalate in the solution, $= \eta'\Lambda/\Lambda_\infty$; $\therefore [C_2O_4''] = \eta'\Lambda N/\Lambda_\infty$. But $\Lambda = 1/RN$. Hence $[C_2O_4''] = \eta'R . R_\infty N_\infty$ or $\log[C_2O_4''] = \log(\eta'/R) + $ constant and the linear relationship assumes the form $\log(\eta'/R) = E/0·029y + $ constant. Measuring the slope of the line we have $1/0·029y = 0·3/0·018$, whence $y = 2$. The complex ion has the formula $Sn(C_2O_4)$

11. The following table gives the E.M.F. at 20°, E, of cells of the type: Tl(Hg), (N_2)/TlCl saturated solution/Tl(Hg), (mol fraction of Tl $= 0·00326$):

N_2	0·01675	·04856	·0986	·1680	·2074	·2701	·3361	·4240
$-E$	0·04555	·08170	·11118	·13552	·1451	·15667	·16535	·17352

Calculate the activity of Tl in the amalgam for which the mol fraction $N_2 = 0·03723$.

From (176) and (115): $\ln a_2/a_2' = -yEF/RT$ or $\log a_2/a_2' = -yE/0·058$ at 20°. Suppose a_2 is the activity of Tl in the amalgam containing a mol fraction N_2 of Tl and let a_2', N_2' ($= 0·00326$) be the corresponding values for the reference amalgam. Then the above equation may be written ($y = 1$): $\log a_2/N_2 = [(-E/0·058) - \log N_2] + \log a_2'$; the quantity $(-E/0·058) - \log N_2$ is plotted against N_2. From

the definition of the standard state (p. 62) $a_2/N_2 = 1$ when $N_2 = 0$; hence the curve intercepts $-\log a_2'$ $(= 2.469)$ on the ordinate $N_2 = 0$. If this value is subtracted from the ordinate at any other value of N_2, $\log a_2/N_2$ is obtained. The ordinate at $N_2 = 0.03723$ is 2.666, whence $a_2/N_2 = 1.574$ and $a_2 = 0.0586$.

By plotting $[(-E/0.058) - \log N_2]$ against N_2/N_1 a graph is obtained which enables $\log a_1/N_1$ to be determined.

EXERCISES.—XXVIII

1. The E.M.F. of the cell Ag/AgCl/ZnCl$_2$, 5H$_2$O/Zn is 1.0171 volt at $0°$ C.; dE/dT is -2.1×10^{-4} volt/$1°$. What is the reaction taking place in the cell? What is the heat of this reaction in g. cal.?

2. The E.M.F. of the combination Cl$_2$/fused PbCl$_2$/Pb is $E = 1.263 - [0.000679(t - 498)]$ volts, where t is the temperature in $°$C. Calculate the heat of formation of PbCl$_2$ at $498°$ C. (Lond. B.Sc. Hons., 1921.)

3. The E.M.F. of the cell Hg, Hg$_2$O/KOH//KCl/HgCl, Hg is 0.1483 volt at $18°$. If the temperature coefficient of the cell is $+ 8.37 \times 10^{-4}$ volt/$1°$, calculate in g. cal. the heat of the reaction HgCl $+$ KOH $= \frac{1}{2}$Hg$_2$O $+ \frac{1}{2}$H$_2$O $+$ KCl.

4. The reaction taking place in the Weston standard cell [Hg/ Hg$_2$SO$_4$/CdSO$_4$ (saturated solution)/CdSO$_4$, $\frac{8}{3}$H$_2$O/Cd (12.5 per cent amalgam)] is Cd (12.5 per cent amalgam) $+$ Hg$_2$SO$_4$ $+ \frac{8}{3}$H$_2$O $=$ CdSO$_4$. $\frac{8}{3}$H$_2$O (s) $+$ 2Hg. If the E.M.F. of the cell at t ($°$C.) is $E = 1.0186 - 0.000038\ (t - 20) - 0.0_6 65\ (t - 20)^2$, calculate the heat of the above reaction in joules at $25°$.

5. The E.M.F. of the cell Hg/Hg$_2$SO$_4$/CdSO$_4$ solution/Hg(Cd)x, where $x =$ atomic percentage of Cd in the amalgam, is, for $x = 1.99$, 1.00910 volt at $25°$ and 0.98349 volt at $75°$, and for $x = 100$, 1.08106 volt and 1.06573 volt, respectively. Calculate the heat in g. cal. of amalgamation of Cd to form a 1.99 per cent amalgam at $50°$.

6. The E.M.F. of the cell Hg, HgCl/HCl $(0.1M)$/Pt (H$_2$; 1 atm.) is given by the equation $E = 0.0964 + 0.001881T - 0.0_5 29\ T^2$. The heat of formation of calomel from its elements is $31{,}300$ g. cal/mol. Calculate the heat of formation at $18°$ of HCl in $0.1M$ solution from its elements.

7. Calculate the E.M.F. of the cell Ag/AgNO$_3$ in MeOH ($v = 40$ l./mol)/AgNO$_3$ in MeOH ($v = 160$ l./mol)/Ag at $0°$. The molecular conductivities of the electrolytes are 39.71 and 53.42 respectively, in Kohlrausch units. The ionic mobilities are: Ag$^{\cdot}$, 16.4; NO$_3'$, 23.3.

8. The E.M.F. at $25°$ of the cell Ag/AgNO$_3$ $(0.1N)$/AgNO$_3$ $(0.01N)$/ Ag, the solvent being EtOH, is 0.0408 volt. The equivalent conductivities of the solutions are 10.81 and 22.06, respectively. Calculate the transport number of the anion in the cell.

9. The measured E.M.F. of the cell Ag/AgCl, HCl(c_1)/AgCl, HCl(c_2)/Ag, where $c_1 = 0.008315$ and $c_2 = 0.001665$ mol/l. is 0.06487 volt. The transport number of the kation is 0.833. What is the E.M.F. after eliminating the diffusion potential?

10. Calculate the E.M.F. at $25°$ of the cell $Ag/AgNO_3(c_2)$ in $MeOH/AgNO_3(c_1)$ in $MeOH/Ag$ from the following data. The ionic mobilities are: NO_3', 30.96; $Ag^{.}$, 22.46; $v_2 = 1/c_2 = 160$ l./mol; $v_1 = 640$ l./mol; the molecular conductivities are $\mu(v_1) = 88.22$ ohm^{-1} and $\mu(v_2) = 70.36$ ohm^{-1}.

11. The E.M.F. at $25°$ of the cell Hg/Hg_2Cl_2, $0.1N$ KCl/$0.1N$ NaOH + HgO/Hg is 0.1518 volt. The potential of the $0.1N$-calomel electrode is $+0.3350$ volt at $18°$ and its dE/dT is 0.00079 volt/$1°$. Assuming the following mobilities at $25°$, calculate the potential of the electrode Hg/HgO $0.1N$ NaOH: Na$^{.}$, 51.0; K$^{.}$, 74.5; OH$'$, 195.9.

12. The potential of the H_2 electrode in N NaOH is -0.814 volt at $0°$ and -0.809 volt at $25°$. Similarly, the potential of the electrode Hg/HgO N NaOH is 0.1162 volt at $0°$ and 0.1135 volt at $25°$. Calculate the heat of the reaction $H_2 + HgO = Hg + H_2O$ at $18°$ in g. cal.

13. The hydrolysis of aniline hydrochloride proceeds according to the equation: $PhNH_2$, $HCl + H_2O = PhNH_3OH + HCl$. The E.M.F. at $25°$ of the cell N-calomel electrode/NH_4NO_3/$PhNH_2$, HCl $(v = 16$ l./mol$)/Pt(H_2)$ is 0.4567 volt. Taking the absolute potential of the calomel electrode as $+0.56$ volt and the absolute standard hydrogen potential as $+0.277$ volt, calculate the degree of hydrolysis of the solution, assuming the acid to be completely dissociated and the base to be non-dissociated.

14. The E.M.F. of the cell $Ag/0.1N$ $AgNO_3$/saturated $KNO_3/0.1N$ KCl saturated with AgCl/Ag is 0.44 volt at $18°$. The degrees of dissociation of the $AgNO_3$ and KCl solutions are 82 per cent and 85 per cent respectively. Calculate the solubility of AgCl in g. per 100 c.c. of pure water. (Manc. Hons. Chem., 1919.)

15. The E.M.F. of the cell $Hg/HgCl/0.1M$ $HCl/Pt(H_2)$ is 0.3985 volt at $25°$ when the moist H_2 is at 1 atm. If the vapour pressure of water at $25°$ is 23.76 mm., calculate the true E.M.F. of this cell when the partial pressure of the H_2 is 1 atm.

16. The E.M.F. of the cell $Pt(H_2$; 1 atm.$)/HCl$ $(0.1N)//NaOH$ $(0.1N)/Pt(H_2$; 1 atm.$)$ is 0.6950 volt at $18°$. The degree of dissociation of the acid is 0.888 and that of the alkali 0.892. Calculate K_w for water at $18°$.

17. Calculate the dissociation pressure of Cu_2O at $17°$ if the E.M.F. of the cell Pt $(O_2$; 1 atm.$)/KOH$ $(0.1N)/Pt$ $(H_2$; 1 atm.$)$ is 1.232 volt and that of the cell $Cu/Cu_2O + KOH$ $(0.1N)/Pt$ $(H_2$; 1 atm.$)$ is 0.469 volt.

18. The dissociation pressure of Ag_2O is 5.0×10^{-4} atm. at $25°$. Calculate the E.M.F. of the cell Pt $(O_2$; 1 atm.$)/Ag_2O$ saturated solution/Ag_2O, Ag.

19. The E.M.F. of the cell Hg/HgO, $0.1N$ alkali/Pt $(H_2$; 1 atm.$)$ is 0.925 volt at $18°$. The ionization constant of water is 0.56×10^{-14} at this temperature. Calculate the solubility product of $Hg(OH)_2$. If the E.M.F. of the oxy-hydrogen cell (gases at 1 atm.) is 1.232 volt at $18°$, calculate the dissociation pressure.of HgO. Calculate also the affinity of O_2 for Hg to form HgO

20. The potential of the electrode Pb/PbO N NaOH is -0.562 volt at $25°$ and that of the electrode Pt $(H_2;$ 1 atm.$)/N$ NaOH is -0.809 volt. The E.M.F. of the cell Pt $(O_2;$ 1 atm.$)/N$ NaOH/Pt $(H_2;$ 1 atm.) is 1.226 volt at $25°$. Calculate the dissociation pressure of red PbO at this temperature. If the heat of dissociation of PbO is $100,600$ cal./mol of O_2, calculate approximately the temperature at which PbO decomposes in air (21 per cent of O_2 by vol.).

21. The equilibrium constant of the reaction $Ag^. + 2NO_2' = Ag + NO_3' + NO$ is $K = [NO_3']p_{NO}/[Ag^.][NO_2']^2 = 1.9 \times 10^5$ at $55°$, p_{NO} being expressed in atm. The heat of the reaction is 1600 cal., absorbed. Suggest a combination in which the above reaction might occur. If the standard potential for $Ag \rightarrow Ag^.$ is $+0.800$ volt at $25°$, calculate the standard potential for the process $2NO_2' \rightarrow NO_3' + NO$.

22. Calculate the potential of the electrode $N_2 \rightarrow 2NO$ in acid and in alkaline solution from a consideration of the E.M.F. of the hypothetical cell N_2, NO/N $H^./Pt$ $(H_2;$ 1 atm.) in which the reaction $N_2 + 2H_2O \rightarrow 2NO + 2H_2$ occurs, given that K_p, the equilibrium constant of the reaction $N_2 + O_2 = 2NO$, is given by $\log\sqrt{K_p} = +0.5442 - 4725.6/T$. The E.M.F. of the cell Pt $(O_2;$ 1 atm.$)/N$ $H^./Pt$ $(H_2;$ 1 atm.) is 1.232 volt at $25°$; $K_w = 1.14 \times 10^{-14}$ at $25°$.

23. The E.M.F. of the cell $Ag + AgCl(s)/HCl$ $(0.01M)/Pt$ $(H_2;$ 1 atm.) is 0.4665 volt at $25°$, the activities of the $H^.$ and Cl' ions in the acid solution being each 0.0093. The E.M.F. of the cell $Ag + AgCl(s)/CdCl_2$ solution $(c = 0.0007M)/Cd$ is 0.9199 volt. If the degree of dissociation of the $CdCl_2$ solution is 0.948, calculate the standard potential of the Cd electrode.

24. The E.M.F. of the cell $Ag + AgCl(s)/ZnCl_2$ solution $(0.000794M)/Zn$ is 1.2442 volt at $25°$, the $ZnCl_2$ solution being dissociated 93.7 per cent. Assuming necessary data in the previous exercise, calculate the standard potential of Zn.

25. The equilibrium constant of the reaction $PbCl_2(s) + Cl_2(g) + Cl'(M) = PbCl_5'(M)$ is 0.070 at $25°$, whilst the E.M.F. of the cell Cl_2 (1 atm.)$/Cl'(M)//H^.(M)/H_2$ (1 atm.) is 1.356 volt at $25°$. The solubility product of $PbCl_2 = [Pb^{..}][Cl']^2 = 0.0_4418$. Calculate the reduction potential of the combination $Pb^{..}(M) + Cl'(M) + PbCl_5'(M)$. [Hint.—The reaction with equilibrium constant 0.07 occurs in the cell $PbCl_2(s)/PbCl_5'(M) + Cl'(M)$ $Cl'(M)/Cl_2$ (1 atm.)].

26. Calculate the equilibrium constant of the reaction $2FeCl_2 + H_3AsO_4 + 2HCl = 2FeCl_3 + H_3AsO_3 + H_2O$ if the standard potential of the electrode $Fe^{..} \rightarrow Fe^{...}$ is $+0.75$ volt and that of the electrode $AsO_3^{...} \rightarrow AsO_4^{...}$ is $+0.61$ volt.

27. Calculate the initial E.M.F. at $20°$ of the cell Cu (CO; 1 atm.)$/OH'$ $(c = 1)$, CO_3'' $(c_1 = 0.01)/Cu$ (air), in which the reaction $2CO + O_2 = 2CO_2$ occurs. Air contains 21 per cent of O_2 by vol. The absorption coefficient of CO_2 is 0.878 and its normal density is 1.9652 g./l. at $20°$; $K_w = 0.76 \times 10^{-14}$ at $20°$ and, for H_2CO_3, $K_1 = 3 \times 10^{-7}$, $K_2 = 6 \times 10^{-11}$. The affinity of the cell reaction is $61\,800$ cal./mol of CO_2 at $20°$.

28. Calculate the approximate temperature at which red PbO will dissociate in air (21 per cent O_2 by vol.). The E.M.F. of the cell Pb/red PbO + N NaOH/Pt (H_2; 1 atm.) is 0·2469 volt at 25° and 0·2063 volt at 0°. The E.M.F. of the cell Pt (O_2; 0·21 atm.)/N NaOH/ Pt (H_2; 1 atm.) is 1·991 volt at 25° and dE/dT is −0·000956 volt/1°, independent of T.

29. The standard potential of the electrode at which the reaction $NO_2' \rightarrow NO_2 - \oplus$ occurs is +0·90 volt and that of the electrode $NO_2 + 2OH' = NO_3' + H_2O - \oplus$ is − 0·88 volt. Show that NO_2 is converted by alkali almost completely into nitrite and nitrate.

30. The standard potential of I_2 ($2I' = I_2 - 2 \oplus$) is + 0·54 volt and that of the reaction $2NO_2' = N_2O_4 - 2 \oplus$ is + 0·875 volt. The solubility product of $AgNO_2$ is 1·6 × 10^{-4} and that of AgI is 1 × 10^{-16}, both at 25°. Show that the reaction $2AgNO_2 + I_2 = 2AgI + N_2O_4$ proceeds to completion at this temperature. [Hint: A suitable hypothetical combination is $I_2(s)$, AgI(s), $AgNO_2$ solution/ $AgNO_2(s)$, $N_2O_4(g)$].

31. The E.M.F.'s at 25° of the cell Co/CoCl₂ (0·05M) + NH₄OH (xM)/NaOH(M) + HgO/Hg, are given below for various concentrations of ammonia, x. The potential of the electrode Hg, HgO, NaOH(M)/KCl(M) is + 0·142 volt at 25°. The standard potential of Co is E(Co $\rightarrow$ Co··) = − 0·237 volt. Assuming the equilibrium Co·· + nNH₃ $\rightleftharpoons$ Co(NH₃)n·· to exist, calculate the value of n. The partial pressure of NH₃ over the solution is p mm.

x =	6	4	3	2
E =	−0·715	−0·693	−0·659	−0·620
p =	107·7	63·4	44·7	27·8

32. The E.M.F. of a cell in which the reaction H_2 (1 atm.) + F_2 (1 atm.) = 2HF (62 mm.) is occurring is 1·468 volt at 248° C. Show that ΔZ for HF at this temperature and 1 atm. is −31,125 cal.

33. If ΔZ for liquid H_2O is −56,560 cal. and that for PbO is −45,050 cal. at 25°, calculate the E.M.F. of the cell in which the reaction PbO(s) + H_2 (1 atm.) = $H_2O(l)$ + Pb(s) is taking place.

34. According to *Luther's rule* if the lowest, intermediate, and highest stages of oxidation of a substance be denoted by l, m, and h, and if a, b are the valencies of the two ions, and $E_1(l \rightarrow h)$, $E_1(l \rightarrow m)$, and $E_1(m \rightarrow h)$ are the standard electrode potentials, then

$$E_1(l \rightarrow h) = [aE_1(l \rightarrow m) + (b - a)E_1(m \rightarrow h)]/b.$$

The E.M.F. of the cell Ag/Ag·//Fe··· + Fe··/Pt is + 0·0528 volt at 25°, the ions being at unit concentration. Calculate the standard potential for Fe·· $\rightarrow$ Fe···, given the following standard potentials: Ag $\rightarrow$ Ag·, + 0·7995; Fe $\rightarrow$ Fe··, − 0·441.

35. The temperature coefficient of the cell Pb/Pb··/Pb amalgam, Pb is 0·000016 volt/1° and the E.M.F. at 25° is 0·0057 volt. Calculate (a) the latent heat of the cell at 25° C.; (b) the heat of the reaction at this temperature; (c) the entropy change; (d) the change of free energy. (Lond. B.Sc. Hons., 1923.)

CHAPTER VI

Nernst's Heat Theorem

(a) CONDENSED SYSTEMS

(1) Approximate Equations for Condensed Systems.

On the assumption that $Q = Q_0 + aT + bT^2$ for reactions in condensed systems, Nernst's heat theorem gives:

$$Q = Q_0 + bT^2 \quad (190) \qquad \text{and} \qquad A = Q_0 - bT^2, \quad (191)$$

where Q_0 and b are constants; Q is the heat, and A the affinity, of the reaction. These equations are not in agreement with the quantum theory but are useful approximations.

EXAMPLES.—1. The molecular heat of ice is given by the equation $C = 3.0 + 0.0223\,T$ and $\lambda_f = 1440$ cal. at the m.p., this value increasing 9 units per 1°. Find the maximum work * of the reaction $CuSO_4 + H_2O$ (ice) $= CuSO_4, H_2O$ at 18° C., given that the heat capacity of the water of crystallization $= 6.60$ cal./mol at 9°, and the heat of hydration of anhydrous $CuSO_4$ by liquid water is 6460 cal./mol at 18°.

$Q_{H_2O} = 6460$ cal. at 18°, and λ_f for ice $= 1440$ cal. at 0°. Since $d\lambda/dT = 9$, λ_f at 18° is $1440 + 9 \times 18 = 1602$ cal., and $Q_{ice} = Q_{H_2O} - 1402 = 4858$ cal. The application of (54) to the reaction $CuSO_4 + H_2O = CuSO_4, H_2O$ gives $dQ/dT = C_{CuSO_4} + C_{ice} - C_{CuSO_4, H_2O} = C_{ice} - C'$, where $C' = C_{CuSO_4, H_2O} - C_{CuSO_4}$, the heat capacity of the water of crystallization. At 9°, $C' = 6.60$ and $C_{ice} = 3.0 + 0.0223 \times 282 = 9.29$, so that $dQ/dT = 9.29 - 6.60 = 2.69$. But, from (190), $dQ/dT = 2bT$ and so $b = (dQ/dT)/2T = 2.69/2(273 + 9) = 0.00477$. Hence $Q_{ice} = Q_0 + 0.00477\,T^2$. When $T = 273 + 18 = 291$, $Q_{ice} = 4858$: $4858 = Q_0 + 0.00477(291)^2$ or $Q_0 = 4454$ cal. From (191) A $= 4454 - 0.00477\,T^2 = 4050$ cal. at 18°.

2. Calculate the E.M.F. of the cell Pb/PbI_2(saturated solution)/I_2(Pt) at 55° from the following data. The heat of formation of 1 mol of solid PbI_2 is $2 \times 19,900$ cal. at 55°; the atomic heat capacity of Pb is 3.2, of I_2, 6.86, and of PbI_2, 9.85.

Let Q be the heat of the reaction $Pb + I_2 = PbI_2$. Then, from (190), $Q = Q_0 + bT^2$ or $dQ/dT = 2bT = 6.4 + 2 \times 6.86 - 19.70 = 0.4$ at 55° (cf. equation 54). Hence $b = 0.4/2 \times 328 = 0.0006096$,

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* The specific heat of water varies abnormally with T, so that it is usual to calculate the heat of hydration by ice and to extrapolate to temperatures above 0°. The given heat of hydration at 18° refers to liquid water and must first be recalculated with reference to ice.

and $Q = Q_0 + 0.0006096\,T^2$, or since $Q = 2 \times 19,900$ at $T = 328°$ K., $Q_0 = 39,734$. Hence $Q = 39,734 + 0.0006096\,T^2$ per mol of PbI_2 or $Q' = 19,867 + 0.0003048\,T^2$ per *equivalent* of PbI_2; the corresponding affinity, by (191), is $A = 19,867 - 0.0003048\,T^2$, and $E = A\,\text{cal.} = A/23,040$ volt $= 0.863 - 1.3 \times 10^{-18}\,T^2$. At $T = 328°$ K. $E = 0.862\ volt$; the observed value is 0.863 volt.

EXERCISES.—XXIX

1. Find the maximum work of the reaction: $K_4FeCy_6 + 3H_2O$ (ice) $= K_4FeCy_6, 3H_2O$, if the total heat capacity of the water of crystallization in the latter hydrate is 11.75 cal. at $9°$ C. and the heat of hydration of 1 mol of anhydrous salt by liquid water is 1630 cal. at $18°$. Assume data in above example.

2. Assuming data in the previous examples, calculate the affinity at $41°$ of the reaction $BaCl_2 + H_2O(\text{ice}) = BaCl_2, H_2O$, given that the heat capacity of the water of crystallization is 10.67 at $9°$ and the heat of hydration of anhydrous salt by liquid water is 3611 cal./mol at $17°$.

3. The heat of the reaction $\tfrac{1}{2}Pb + AgCl = \tfrac{1}{2}PbCl_2 + 2Ag$ is given by $Q = 11,904 + 0.010062\,T^2 - 0.0_4171\,T^3$. Plot the A and Q curves. A represents the E.M.F. (in cal. $=$ volts $\times 23,040$) of the cell $Ag/AgCl$, $PbCl_2$ (saturated solution)/Pb, in which the above reaction occurs, per faraday. Show that between $0°$ and $100°$ K. the Berthelot-Thomson rule ($A = Q$) is valid for this cell. What is the maximum value of Q?

4. Plot the A-T, Q-T curves for the hydration of anhydrous K_4FeCy_6. Show from the graph that above about $160°$ K. ice and anhydrous K_4FeCy_6 can combine to form a hydrate. Assume the data of Exercise 1.

5. Calculate the E.M.F. of the cell $Pb/PbCl_2(s) +$ saturated solution/$AgCl(s) +$ saturated solution/Ag at $25°$ if the heat of the reaction $\tfrac{1}{2}Pb + AgCl = \tfrac{1}{2}PbCl_2 + Ag$ is given by $Q = 11,904 + 0.010062\,T^2$ cal. (N.B.—This cell, because it contains *saturated* solutions, is a condensed system.)

6. Calculate the E.M.F. of the Clark cell at the cryohydric point ($-7°$ C.): $Zn(s)/ZnSO_4$, $7H_2O(s)/Hg_2SO_4(s)/Hg(l)$. The reaction is $Zn + Hg_2SO_4 + 7H_2O(s) = ZnSO_4 . 7H_2O + 2Hg$. The heat of formation of $ZnSO_4$ is $230,090$ cal. and that of hydration, $22,690$ cal. The mol. heat of fusion of ice is 1580 cal. and the heat of the change $Hg_2SO_4 \longrightarrow 2Hg$ is $-175,000$ cal. The following mol. heats hold at $10°$ (approx.): Zn, 6.0; Hg_2SO_4, 31.0; $H_2O(s)$, 9.1; $ZnSO_4$, $7H_2O$, 89.4; and $2Hg$, 13.2.

7. Calculate the transition temperature of rhombic into monoclinic S, given that the heat of transition, Q, is 2.4 cal./g. at $0°$ and $dQ/dT = 2.3 \times 10^{-5}\,T$.

(2) Exact Calculation of Maximum Work in Condensed Systems.

The integration of (65), with the assistance of (190) and of

(54) (which may be written $Q = Q_0 + \int_0^T \Sigma n C_p \, dT$), gives the exact equation

$$A = Q_0 - T \int_0^T \frac{dT}{T^2} \int_0^T \Sigma n C_p \, dT. \qquad . \quad (192)$$

The application of this equation is facilitated by the use of the functions $\psi = \int_0^T \frac{dT}{T^2} \int_0^T C_p \, dT$ and $\varphi = \frac{1}{T} \int_0^T C_p \, dT$. The values of C_p are usually calculated by means of the specific heat equations on p. 14, and ψ and φ have been tabulated for various values of θ, the characteristic temperature.[*]

(b) Gaseous Systems

(1) An exact formula of the equilibrium constant of a gaseous reaction analogous to (192) may be deduced; its application is not considered here (see Eucken, p. 413). Nernst, however, uses the following approximate equation, which is easily applied:

$$\log K_p = Q_0/4{\cdot}576 \, T + 1{\cdot}75 \, \Sigma n \, \log T \\ + \Sigma n \beta T/4{\cdot}576 + \Sigma n C. \qquad . \quad (193)$$

This equation requires that the heat of the reaction be expressed in the form $Q_p = Q_0 + 3{\cdot}75 \Sigma n T + \Sigma n \beta T^2$ and the specific heats of the reactants [†] in the form $C_p = 3{\cdot}5 + 2\beta T$. In (193), β is a constant, C is a constant (the *conventional chemical constant*, $= 3$ approx.), and Σn represents the number of gaseous molecules on the right-hand side of the equation in excess of the number on the left-hand side. As a rule β is small and (193) may be written

$$\log K_p = Q_p/4{\cdot}576 \, T + 1{\cdot}75 \Sigma n \, \log T + \Sigma n C, \quad (194)$$

where Q_p has been written for Q_0; (194) is an approximation equation of great practical importance.

[*] Miething, *Abh. Deutsch. Bunsengesell.* No. 9; see Eucken, Jette, and La Mer, *Fundamentals of Physical Chemistry*, p. 406.

[†] Equations (193) and (194) apply also to heterogeneous systems. The term $\Sigma(nC)$ then refers to the *gaseous molecules only*; similarly for Σn in the $\Sigma n \log T$ term. But $\Sigma n \beta$ is the algebraic sum of the T-coefficients of the specific heats of *all* the reactants, condensed and gaseous. β is calculated from the equation $\Sigma n C_p = 3{\cdot}5 \Sigma n + 2 \Sigma n \beta T$ by substituting values of C_p for some value of T, midway between the absolute zero and the temperature of the experiment if possible.

(2) Calculation of Chemical Constants.

The value of C in (193), (194) is approximately 3 for most substances. It may be calculated by means of various equations, e.g.:

Cederberg: $\qquad C = 1 \cdot 6 \log p_c.$ . . . . (195)

Nernst: $\qquad C = 1 \cdot 1\, a = 0 \cdot 14 \lambda_e / T_s,$ (196), (197)

where a is the constant in van der Waals' vapour-pressure equation (44), T_s is the b.p. (°K.), and M is the at. wt. Equations for chemical constants are deducible from the quantum theory (see Tolman, *Statistical Mechanics*, 1927), but these values must not be used in (193–4).

<div align="center">VALUES OF C</div>

Hg	1·4	HCl, H_2S, C_6H_6	3·0	HI, C_2N_2 ..	3·4
H_2	1·6	Cl_2, CS_2, CCl_4	3·1	CO, NO ..	3·5
N_2, C_2H_6 ..	2·6	Br_2, HBr, CO_2	3·2	H_2O	3·6
O_2, CH_4 ..	2·8	N_2O, SO_2, NH_3	3·3	I_2	3·9

EXAMPLES.—1. Calculate the equilibrium constants at 500° K. and 1000° K. of the reaction $4NH_3 + 5O_2 = 4NO + 6H_2O$ (g) from the following heats of reaction at 17° C.: $N_2 + O_2 = 2NO - 43,200$ cal.; $2H_2 + O_2 = 2H_2O + 115,860$ cal.; $N_2 + 3H_2 = 2NH_3 + 22,800$ cal., and the following values of C_p: O_2, $6 \cdot 885 + 9 \times 10^{-4}\, t$; NH_3, $8 \cdot 62 + 0 \cdot 0035 t + 5 \cdot 1 \times 10^{-6}\, t^2$; NO, $6 \cdot 885 + 9 \times 10^{-4}\, t$; H_2O, $8 \cdot 05 + 1 \times 10^{-3}\, t + 8 \times 10^{-10}\, t^3$.

The equations for C_p must first be converted into the form $C_p = 3 \cdot 5 + 2\beta T$ so that equation (193) may be applied. Since values of K_p for 500° and 1000° K. are required we shall take 800° as a mean, whence $2\beta = (C_p^{800} - 3 \cdot 5)/800$. For β at 800° K. we have: O_2, 0·0048; NH_3, 0·0105; NO, 0·0048; H_2O, 0·0065. The specific heats can now be written in the required form: O_2, $3 \cdot 5 + 0 \cdot 0048$ T; NH_3, $3 \cdot 5 + 0 \cdot 0105$ T; NO, $3 \cdot 5 + 0 \cdot 0048$ T; H_2O, $3 \cdot 5 + 0 \cdot 0065$ T. These equations are now substituted in Kirchhoff's equation (54) in order to find Q_0: $Q = Q_0 - 3 \cdot 5$ T $+ 0 \cdot 004$ T^2. But Q at 273 + 17 = 290° K. is $3 \times 115,860 - 2 \times 22,800 - 2 \times 43,200 = 215,600$ cal. Hence $Q_0 = 216,300$ cal. Further $\Sigma n = 4 + 6 - 4 - 5 = 1$; $\Sigma nC = 4 \times 3 \cdot 5 + 6 \times 3 \cdot 6 - 5 \times 2 \cdot 8 - 4 \times 3 \cdot 3 = 8 \cdot 4$; and $\Sigma n\beta = 4 \times 0 \cdot 0024 + 6 \times 0 \cdot 00325 - 4 \times 0 \cdot 00525 - 5 \times 0 \cdot 0024 = -0 \cdot 004$. Substitute in (193): $\log K_p = 216,300/4 \cdot 576$ T $+ 1 \cdot 75 \log$ T $- 0 \cdot 004$ T$/4 \cdot 576 + 8 \cdot 4$, whence $\log K_p = 107 \cdot 2$ at 500° K. and 60 at 1000° K.

The approximation equation, (194), gives $\log K_p = 215,600/4 \cdot 576$ T $+ 1 \cdot 75 \log$ T $+ 8 \cdot 4$, from which $\log K_p = 107 \cdot 3$ at 500° and 61 at 1000° K.

2. The heat of dissociation of $SrCO_3$ is 55,770 cal./mol, absorbed, the pressure being 1 atm. Calculate the temperature at which the dissociation pressure is 1 atm.

The reaction is $SrCO_3 \rightleftharpoons SrO + CO_2$; $K_p = p_{CO_2}$ and $\Sigma n = 1$. Hence, from (194), $\log p_{CO_2} = Q/4 \cdot 576\,T + 1 \cdot 75 \log T + 3 \cdot 2 = -55,770/4 \cdot 576\,T + 1 \cdot 75 \log T + 3 \cdot 2$. When $p_{CO_2} = 1$, then $55,770/4 \cdot 576\,T = 1 \cdot 75 \log T + 3 \cdot 2$. This may be solved by plotting $y = 55,770/4 \cdot 576\,T$ and $y = 1 \cdot 75 \log T + 3 \cdot 2$, or by Newton's method; $T = 1400°\ K.$

3. Assuming $p_c = 67$ atm. and $T_c = 268°$ K. for O_3, calculate with the aid of van der Waals' vapour-pressure equation the conventional chemical constant for O_3, given the following vapour pressures:

p (mm.) ..	33·8	101·7	237·3	500·2	840·8
T (°K) ..	120·0	131·7	142·7	154·6	164·7

According to (44) the plot of $\log p_c/p$ against T_c/T yields a straight line, the gradient of which is a, and the intercept on the $\log p_c/p$ axis, $- a$; from (196), $C = 1 \cdot 1a$. By measuring the slope of the graph (p in atm.) it is found that $a = 2 \cdot 64$; this is a mean value over the temperature range considered, since strictly $a = f(T)$. Hence $C = 1 \cdot 1 \times 2 \cdot 64 = 2 \cdot 9.$

EXERCISES.—XXX

1. The heat of dissociation of Ag_2CO_3 is 20,060 cal. (absorbed). At what temperature will Ag_2CO_3 dissociate in a flask of vol. 1 l., into which are introduced, after evacuation, 200 c.c. of CO_2 and 300 c.c. of N_2 measured at N.T.P.?

2. What is the maximum yield of NO obtainable from air at 1800° K. if the heat of the reaction $2NO = N_2 + O_2$ is 43,200 cal., evolved?

3. The heat absorbed in the reaction $2PbO(red) \rightleftharpoons 2Pb + O_2$ is 100,600 cal. Calculate the dissociation pressure of red PbO at 25°. At what temperature will this oxide decompose in air (21 per cent O_2)?

4. The heat of the reaction $H_2 + (CN)_2 = 2HCN$ is $+11,000$ cal. at room temperature. Calculate approximately the equilibrium constant at 300° C., given the following data: HCN: $p_c = 85$ atm., $T_c = 506°$ K., b.p. 299·5° K.; $(CN)_2$: $p_c = 61 \cdot 7$ atm., $T_c = 397°$ K.; vapour pressure at 252° K. = 0·99 atm.

5. From the following heats of reaction: $CCl_4 + 2H_2 = C + 4HCl + 62,570$ cal.; $H_2 + Cl_2 = 2HCl + 44,000$ cal., show that CCl_4 is 40 per cent decomposed at 600° K.

6. The vapour pressure of $NiCl_2$, NH_3 is 223 mm. at 339° C. Show that the approximate heat of dissociation is 21,450 cal./mol.

7. The dissociation pressure of IrO_2 is 1 atm. at 1100° C. Show that the average heat of dissociation is 52,000 cal./mol.

8. Calculate the temperature at which the following reaction will proceed in the air: $2Cu(NO_3)_2 \rightleftharpoons 2CuO + 4NO_2 + O_2 - 2 \times 47,592$ cal. Chemical constants: NO_2, 3·5; O_2, 2·8.

9. The heat of dissociation of $CaCO_3$ is 42,500 cal. ($CaCO_3 = CaO + CO_2 - 42,500$). Find the dissociation pressure of $CaCO_3$

at 1000° absolute, given that the chemical constant for CO_2 is 3·4. (Lond. B.Sc. Special, 1927.)

10. Using (193), calculate the degree of dissociation of CO_2 into CO and O_2 at 1375° K., given that the heat of formation of CO from its elements is 26,300 cal./mol and that of CO_2, 94,300 cal./mol, both at room temperature. Mol. heats, C_p, at 573° K.: O_2, 7·16; CO, 7·16; CO_2, 10·52.

11. The heat of the reaction $SiC + 2CO = SiO_2 + 3C$ is 127,450 cal. Given the following mol. heats at 300° K.: SiC, 6·5; CO, 6·9; SiO_2, 10·8; C (atomic heat), 2·1, calculate the pressure of the system at 1600° K.

12. Calculate the partial pressure of N_2O in the air at 2000° K. from the following data. The heat of the reaction $2N_2O = 2N_2 + O_2$ is 38,000 cal. at room temperature. The mol. heats of N_2 and O_2 at $T = 473°$ K. are both 7·0, and that of N_2O is 10·76 cal.

MISCELLANEOUS EXERCISES

[N.B.—Answers are not supplied to these exercises.]

1. The transport number of Cl′ in LiCl solution containing 0·008 g. equivalent/l. is 0·670 at 18°, and Λ_∞ is 98·88 for this salt. Calculate the velocity of the Li ion in cm./sec. under unit potential gradient.

2. The cell Cu/CuBr, 0·01N KBr/N KNO₃/0·01N KI, CuI/Cu gave, at 23·1° C., an E.M.F. of 0·2041 volt. The temperature coefficient of E.M.F. was −0·000305 volt/1°. Calculate the heat of the reaction $CuBr + KI \longrightarrow CuI + KBr$ for the above concentration. (Lond. B.Sc. Hons., 1919.)

3. Calculate the transport number of Mg from the following results with $MgCl_2$ solution, 10·9018 g. of which yielded 3·5720 g. of AgCl on precipitation. After electrolysis the anode solution weighed 18·1054 g. and yielded 6·4505 g. of AgCl, whilst 0·5836 g. of Ag was deposited in the coulometer.

4. A benzene solution of Et acetate containing 50 g./l. is shaken at 12° C. with half its vol. of distilled water until equilibrium is established. Given that the partition coefficient between benzene and water [i.e. (concentration in C_6H_6)/(concentration in H_2O)] is 10·7 at 12°, what difference should be found between the f.p. of the aqueous layer and that of distilled water? Mol. depression constant for water = 18·6°, referred to 100 g. (Lond. B.Sc. Hons., 1922.)

5. A defective barometer reads 745 mm. when the true pressure is 756 mm. and 751 mm. when the true pressure is 764 mm. What will it read when the true atmospheric pressure is 774·5 mm.?

6. If 14·93 mols of HI are formed when 14·44 mols of I_2 and 8·12 mols of H_2 are heated at 717° K., find how many mols of HI are formed if the experiment is started with 33·10 mols of I_2 and 7·89 mols of H_2.

7. A conductivity vessel when filled with $0.1N$ KCl has a resistance of 17.86 ohms; when filled with $0.0002N$ KCl the resistance of the same vessel is 7770 ohms; and with $0.0001N$ KCl it is 15,500 ohms. Calculate approximately the f.p. of the $N/10$ KCl solution; the f.p. of a 1 per cent cane-sugar solution is $-0.0544°$. The resistance of the water is supposed to be infinite. (Lond. B.Sc. Hons., 1911.)

8. If N_2O_4 is 91 per cent dissociated at $49.7°$ C. and 26.8 mm. pressure, calculate the degree of dissociation at the same temperature but under a pressure of 497.8 mm.

9. The b.p. of $CHCl_3$ was raised $0.575°$ by the solution of 1.920 g. of naphthalene in 100 g. Calculate the mol. elevation constant for $CHCl_3$.

10. The thermal dissociation of. $CoSO_4$ at $1208°$ K., $CoSO_4 \rightleftharpoons CoO + SO_3$; $2SO_3 \rightleftharpoons 2SO_2 + O_2$ causes a total pressure of 525 mm. to be developed. If $\log[SO_2]^2[O_2]/[SO_3]^2 = -10,373/T - 2.222 \log T + 14.585$, calculate the partial pressure of the O_2.

11. The substance X decomposes slowly when dissolved in water. A solution was found to have the following normalities at the times stated after making up:

t (min.) ..	0	10	50	100	150
N	1.0000	0.9616	0.8235	0.6776	0.5572

Find the order of the reaction and the time at which the decomposition would have amounted to 50 per cent. (Manc. Hons. Chem., 1926.)

12. At $10°$ C. the electrolytic dissociation constant of MeCOOH is 1.79×10^{-5} and at $40°$ C. it is 1.87×10^{-5}. Calculate the heat of ionization of the acid at $25°$ C. (Lond. B.Sc. Hons., 1921.)

13. The latent heat of fusion of ice at the m.p. is 79.74 cal./g. Calculate the degree of dissociation of a solution of 1.125 g. of K_2CO_3 in 1000 g. of water which freezes at $-0.0577°$.

14. For N_2, $p_c = 33.5$ atm. and $T_c = 126.0°$ K. The density is 1.2507 g./l. at S.T.P. Calculate the critical density ($N = 14.00$). Use van der Waals' equation.

15. In the hydrolysis of propyl acetate in the presence of dilute HCl in dilute aqueous solution the following data were recorded:

Time from start in minutes ..	..	60	350
Percentage of ester decomposed	..	18.17	69.12

Calculate the time in which half the ester was decomposed. (Lond. B.Sc. Hons., 1921.)

16. Calculate the E.M.F. of the following concentration cell: $Cu/CuSO_4$ solution (2.807 g./l.)$//CuSO_4$ solution (1.069 g./l.)/Cu if the f.p. of the concentrated solution is $-0.0475°$ and that of the dilute solution $-0.02°$. $L_f = 79.74$ cal./g. for water at $0°$.

17. The true specific heat of Pb is given by $c = 0.0297 + 0.0_41358t$, where t is in degrees C. Calculate the mean specific heat over the range $0° - 200°$ C. What heat is absorbed in heating 5 g. of Pb from $15°$ to $120°$ C.?

18. Calculate the standard affinity of O_2 for Ni if the dissociation pressure of NiO is $5 \cdot 181 \times 10^{-26}$ mm. at $450°$ C.

19. Show that acetanilide hydrochloride is completely hydrolysed in solution at $25°$ from the following distribution ratio results. $0 \cdot 3280$ mol of HCl and $0 \cdot 0288$ mol of acetanilide were dissolved in 1 l. of water and the solution shaken with 59 c.c. of C_6H_6. The concentration of free base in the C_6H_6 layer was $5 \cdot 802$ mol/l. The distribution ratio of acetanilide between C_6H_6 and water is $1 \cdot 653$.

20. The Na salt of a monobasic acid was found to be hydrolytically dissociated to the extent of $1 \cdot 71$ per cent in aqueous solution at a dilution of 32 l. at $25°$ C. Calculate the dissociation constant of the acid for this temperature. $K_w = 1 \cdot 2 \times 10^{-14}$ at $25°$. (Lond. B.Sc. Hons., 1911.)

21. Calculate the degree of dissociation of CO_2 into CO and O_2 at $2200°$ if $\log K_c' = \log[CO_2]^2/[CO]^2[O_2] = 6 \cdot 4269$ at this temperature.

22. Calculate the value of K_h for $CoSO_4$ from the following data. The E.M.F. of the cell $H_2/CoSO_4$ $(v = 8)/NH_4NO_3/N$-cal. electrode is $-0 \cdot 5675$ volt. The absolute potential of the N-calomel electrode and the absolute standard electrode potential of H_2 are, respectively, $+0 \cdot 56$ and $+0 \cdot 277$ volt. The base produced is assumed to be undissociated and the acid is considered to be completely dissociated.

23. For C_6H_6 λ_f is 2370 cal./mol at the f.p., $5 \cdot 480°$. Calculate the f.p. of C_6H_6 containing a mol fraction $0 \cdot 04270$ of benzyl benzoate, assuming the system to be ideal.

24. By two distinct reactions Thomsen determined the heat of formation of HClO. From the following data calculate the heat of formation of an aqueous solution of HClO as determined by both methods: (2NaOH aq., Cl_2)* = 24,647; (NaOH aq., HCl aq.) = 13,470; (NaOH aq., HClO aq.) = 9976; (H, Cl, aq.) = 39,315; (H_2, O) = 68,357; (HClO aq., 2HI aq.) = 51,435; (H, I, aq.) = 13,171 cals. (Lond. B.Sc. Hons. (Ext.), 1904.)

25. A solution of $CuSO_4$ containing $0 \cdot 0808$ per cent of Cu was electrolysed between suitable electrodes. After $0 \cdot 6607$ g. of Ag had been deposited in the voltameter the anode solution was run off. It weighed $320 \cdot 980$ g. and contained $0 \cdot 11864$ per cent of Cu. Show that the transport number of Cu is $0 \cdot 375$.

26. The dissociation constant of NH_4OH in aqueous solution at $25°$ C. is $1 \cdot 8 \times 10^{-5}$, and the dissociation constant of water is $0 \cdot 8 \times 10^{-14}$. A solution, $0 \cdot 02N$ with respect to NH_4OH and $0 \cdot 01N$ with respect to a monobasic organic acid, has a H ion concentration of $1 \cdot 6 \times 10^{-10}$ equivalent/l. Calculate (a) the dissociation constant of the acid; (b) the percentage hydrolyses of $0 \cdot 001N$ and $0 \cdot 1N$ solutions of the ammonium salt; (c) the percentage hydrolyses of $0 \cdot 001N$ and $0 \cdot 1N$ solutions of the Na salt. (Lond. B.Sc. Special, 1926.)

27. The heat of the reaction $H_2 + S(s) = H_2S$ is 5000 cal. evolved (approx.). Find an expression for K_p. Chemical constants: H_2, $1 \cdot 6$; H_2S, $3 \cdot 0$.

* The heat of reaction of Cl_2 with 2NaOH in aq. solution is 24,647 cal., &c.

28. The dissociation constant of H_2O is $0 \cdot 09 \times 10^{-14}$ at $0°$ and $4 \cdot 5 \times 10^{-14}$ at $50°$. Calculate the heat of ionization at $25°$ C.

29. The E.M.F. of the cell $Pt(Br_2)\,/\,PbBr_2$ (fused) $/Pb$ is E $= 1 \cdot 0945 - 0 \cdot 000714\ (t - 367)$. Calculate the heat of formation of $PbBr_2$ from its elements at $498°$ C.

30. Calculate the weight of CO_2 under a pressure of 6 atm. which will dissolve in 2 l. of water at $0°$. Solubility coefficient is $1 \cdot 8$.

31. The dissociation pressures of amorphous Ag_2CO_3 are as follows:

p (mm.) ..	234	299	401	529	630	902
T	182·5	191	196	203·5	208	217

Calculate the heat of dissociation at $196°$. Find the dissociation temperature under a pressure of 600 mm.

32. Calculate the percentage composition and mol. wt. of a substance that gives the following results on analysis: (1) $0 \cdot 2$ g. of the substance gave $0 \cdot 687$ g. of CO_2 and $0 \cdot 1125$ g. of H_2O; (2) $0 \cdot 0925$ g. of the substance dissolved in 10 g. of C_6H_6 gave $1 \cdot 037°$ depression of the f.p. Coefficient for $C_6H_6 = 49$, referred to 100 g. of the solvent. (Lond. B.Sc. Hons., 1923.)

33. Assuming the ideal mol. vol. to be $22 \cdot 415$ l., calculate the mol. wt. of $(CH_3)_2O$ vapour if its normal density is $2 \cdot 10960$, and its coefficient of compressibility, $0 \cdot 02656$.

34. A saturated solution of AgCl had a specific conductivity of $1 \cdot 33 \times 10^{-6}$ ohm^{-1} at $20°$. If $\Lambda_\infty = 125 \cdot 5$, calculate the solubility product of AgCl.

35. At $0°$ C. the vapour pressure of water $= 4 \cdot 62$ mm., and that of a solution of $2 \cdot 28$ g. of $CaCl_2$ in 100 g. of water $= 4 \cdot 584$ mm. Calculate the degree of dissociation of the salt. (Lond. B.Sc. Special, 1926.)

36. The specific heat of C_6H_6 at constant pressure is $0 \cdot 4250$ cal./$1°$ at $25°$. The molecular volume of C_6H_6 at the same temperature is $88 \cdot 8$ c.c., whilst the coefficient of expansion is $0 \cdot 00124$ per $1°$ and the isothermal compressibility is $0 \cdot 000098$ megabar^{-1}. Calculate c_v in cals./$1°$.

37. If the vapour pressure of Hg is given by $\log p$ (mm.) $= 9 \cdot 907 - 3276 \cdot 6/T - 0 \cdot 652\ \log T$, calculate the latent heat of evaporation per mol at $400°$ C.

38. The mean specific heats of Pb are $0 \cdot 0310$ between $100°$ and $18°$; $0 \cdot 0300$ between $18°$ and $- 79°$; and $0 \cdot 0291$ between $- 79°$ and $- 186°$. Calculate the mean specific heat of Pb between $- 186°$ and $100°$ and find the heat absorbed when 1 Kgm. of Pb is heated from $18°$ to $78°$ C.

39. The E.M.F. of the cell Pt/NEt_4I in MeOH ($v = 16$ l./mol)/ NEt_4I in MeOH($v = 64$ l./mol)/Pt is $0 \cdot 0126$ volt at $25°$. The mol. conductivities of the solutions are $68 \cdot 3$ and $83 \cdot 8$ ohm^{-1}, respectively. Calculate the transport number of the kation.

40. The m.p. of MeCOOH is $16 \cdot 6°$ C.; its heat of fusion is $46 \cdot 42$ cal. [per g.] and the value of dT/dp is $0 \cdot 0242°$ [per atm.]. Calculate the change in volume when 1 g. of solid MeCOOH is melted. (Lond. B.Sc. Hons., 1908.)

41. A gas under certain conditions is found to polymerize, so that 1 vol. of the original gas yields half that volume of the polymer. In an experiment which was carried out at constant temperature and volume the pressure of the gas fell in 1 hr. to 0·8600 and in 8 hr. to 0·5359 of its original value. What is the order of the reaction and what deductions can you draw with respect to the mechanism of the polymerization? (Manc. Hons. Chem., 1921.)

42. 0·5 g. of $NaHCO_3$ was introduced into a vessel of volume v and at a temperature of 250°. The pressure increase was 10·2 cm. Calculate v.

43. From the electrolysis of HCl in a cell with a Cd anode the following results were obtained: change in concentration of Cl at anode and kathode, respectively, $\pm$ 0·00545 g.; Ag deposited in voltameter connected in series with the cell, 0·0986 g. Calculate the transport numbers of H˙ and Cl′. (Lond. B.Sc. Hons. (Ext.), 1909.)

44. The vapour pressure of alumina at 2858° K. is 55 mm., and at 2632° K. 9·5 mm. Calculate the mean mol. heat of evaporation.

45. For O_2, $Tc = 154·2°$ K. and $pc = 50·8$ atm. Calculate the van der Waals constants, a and b. If Avogadro's number is $6·06 \times 10^{23}$, calculate approximately the diameter of the O_2 molecule.

46. The E.M.F. of the cell $Hg/Hg_2Cl_2//HCl(c)/H_2$ (1 atm.) is $E = 0·39884 [1 + 386 \times 10^{-6} (t - 25)]$, t being the temperature in °C., when $c = 0·1004$ molal. What reaction is taking place in this cell, and what is the heat of this reaction?

47. The heat of formation of CO_2 at constant pressure from CO and $\frac{1}{2}O_2$ at 0° C. is 68,000 cal. The true mol. heats at constant vol. of the gases at T° absolute are: CO_2, $5·106 + 0·00334\,T$; CO and O_2, $4·68 + 0·000268\,T$. Find the heat of formation of CO_2 at constant pressure at 1000° C. (Lond. B.Sc. Hons., 1923.)

48. Given that for a certain monobasic acid the dissociation constant $K = 6·0 \times 10^{-5}$ (for v in l.) and $\Lambda_\infty = 381$, both at 25° C., calculate the resistance at this temperature of a cylindrical column of a $N/50$ solution of the acid, 3 cm. in length and 2 cm. in diameter. (Lond. B.Sc. Hons., 1924.)

49. At 0° it was found that CO_2 is taken up by charcoal as follows, p being the pressure of gas when equilibrium is established and c being the concentration of the gas in the solid:

c			0·77	1·45	2·02	2·48
p			25·1	137·4	416·4	858·6

What conclusions might be drawn from these results? (Lond. B.Sc. Hons. (Ext.), 1911.)

50. The E.M.F. of the cell Hg/Hg_2Cl_2, $0·01N$ KCl, N $KNO_3/$ N $KNO_3/0·01N$ KI, Hg_2I_2 (yellow), N KNO_3/Hg is + 0·3131 volt at 0° and $dE/dT = -0·00027$ volt/1°. Calculate (a) the latent heat of the cell at 0°; (b) the entropy change; (c) the heat of the reaction; and (d) the free energy change.

51. The surface tension of water is 74·12 at 10° and 71·12 at 30°;

the densities at these temperatures are 0·999727 and 0·995673, respectively. What is the degree of association of water?

52. Given that the dissociation constant of acetic acid at 18° is 0·000018 (vol. expressed in l.), calculate the H˙ concentration in a $N/5$ solution of the acid. How much Na acetate (approx.) would have to be added to 1 l. of this solution in order to reduce the H˙ concentration to one-tenth of its original value? It may be assumed that the Na acetate is completely ionized in solution. (Lond. B.Sc. Hons., 1922.)

53. The b.p. of PhCl is 405° K. and dp/dT at this temperature is 20·5 mm./1°. The density of the liquid is 0·9814 and that of the saturated vapour 0·00359, both at the b.p. Calculate L_e.

54. A solution of BaI_2 containing 1·25 millimols of salt in 10 c.c. is treated with b millimols of I_2. The solution is found by partition experiments to contain x millimols of free I_2 per 10 c.c. What conclusions can you draw as to the state of BaI_2 in aqueous I_2 solution from the following results of 2 experiments: $b = 0·07048$, $x = 0·00043$; $b = 0·09810$, $x = 0·00060$?

[The equilibrium $BaI_2 + I_2 \rightleftharpoons BaI_4$ is set up. $K = [BaI_2][I_2]/[BaI_4] = [a - (b - x)]x/(b - x) = 0·0071$.]

55. The density of methyl fluoride at S.T.P. is 1·54507 and that of O_2 is 1·42882. The respective compressibility coefficients are 0·01802 and 0·00097. What is the at. wt. of F?

56. The second dissociation constant of H_2CO_3 is $6·0 \times 10^{-11}$ and the solubility product of $CaCO_3$ is $(1·45)^2 \times 10^{-8}$. The first dissociation constant of H_2CO_3 is $3·04 \times 10^{-7}$. The molecular coefficient of absorption of CO_2 by water is 0·043 at 15° to 16°. Show that for this temperature the solubility of $CaCO_3$ in CO_2 solution is given by $0·0105 \sqrt[3]{p}$, where p is the partial pressure of CO_2 in the gas phase.

57. The solubility of I_2 in 1000 g. of water is 0·3395 g. at 25° and 0·4661 g. at 35°. The molecular heat of evaporation of I_2 is 15,100 cal. (approximately independent of T between 0° and 55°). Calculate the molecular heat of solution of I_2 and the molecular heat of evaporation from solution, both at 30°.

58. The resistance of a cell filled with KCl solution containing 1·49 g./l. and having a specific conductivity of $2·768 \times 10^{-3}$ ohm^{-1} is 202·6 ohms. When filled with a solution of NaSCN in alcohol containing 0·4175 g. of salt in 50 c.c. the resistance of the cell is 252·05 ohms. Find the molecular conductivity of the thiocyanate solution. (Lond. B.Sc. Special, 1927.)

59. The molecular elevation in b.p. per 100 c.c. of C_6H_6 is 32·8. Calculate the mol. wt. of cholesterol in C_6H_6 if 0·788 g. in 15·12 c.c. caused a b.p. elevation of 0·32°.

60. The vapour pressures of ClO_2 at 10° C. and 10·2° C. are 732 mm. and 769 mm., respectively. Calculate the latent heat of evaporation per g. mol (ClO_2) of the substance at 10·6°, and assuming that this has the same value at the b.p., 11° C., calculate the Trouton coefficient. What conclusion may be drawn from the value of the latter? (Lond. B.Sc. Special, 1927.)

61. The isothermal compressibility of CCl_4 is $89\cdot6 \times 10^{-6}$ megabar^{-1}. By how much does 10 l. of CCl_4 decrease in volume when the pressure is raised from 1 atm. to 100 atm.?

62. Calculate the osmotic pressure of a $0\cdot1N$ solution of NaCl at 18° C. The molecular conductivity of this solution at 18° is 92 ohm^{-1} and that of the salt at infinite dilution 109 ohm^{-1}. (Camb. Nat. Sci. Tripos, 1915.)

63. At 2000° C. and 1 atm. pressure CO_2 is dissociated into CO and O_2 to the extent of 4 per cent; calculate the equilibrium constant and the affinity of the reaction: 2 g. mols. of CO + 1 g. mol. of $O_2 \longrightarrow$ 2 g. mols. of CO_2, performed at 2000° C. in a vessel of 5 l. capacity. Assume the gm. mol. vol. to be $22\cdot4$ l. at S.T.P. (Manc. Hons. Chem., 1922.)

64. The concentration of a reacting substance decreased at the following rate. The times are reckoned in minutes from the *beginning* of the reaction:

t	0	15	25	45
concentration ..	$0\cdot1600$	$0\cdot0597$	$0\cdot0421$	$0\cdot0265$

Determine the order of this reaction. (Manc. Hons. Chem., 1920.)

65. The surface tension of C_3H_8 at the b.p., $-44\cdot5°$, is $15\cdot63$ dynes/cm. The value at $-71°$ is $19\cdot63$ dynes/cm. If the density of the liquid at these respective temperatures is $0\cdot5853$ and $0\cdot6155$, state whether the liquid is associated over this temperature range.

66. The dissociation constant of benzoic acid at 25° is 6×10^{-5} and its solubility $3\cdot4$ g./l. Calculate its solubility in $0\cdot01N$ Na benzoate solution (completely dissociated).

67. The pressure on 8 l. of H_2 at 15° and 1 atm. is suddenly increased to 10 atm. Calculate the final vol. and temperature. $C_p/C_v = 1\cdot405$.

68. For N_2, $p_c = 33\cdot5$ atm. and $T_c = 126\cdot0°$ K. Calculate the values of a and b in van der Waals' equation.

69. Calculate ΔH for the oxidation of Zn: $ZnO + H_2O = Zn(OH)_2$, $\Delta H = -2400$; $Zn(OH)_2 + 2HCl$ aq. $= ZnCl_2$ aq. $+ H_2O$, $\Delta H = -19{,}483$; $H_2 + \frac{1}{2}O_2 = H_2O$, $\Delta H = -68{,}380$; $Zn + 2HCl$ aq. $= ZnCl_2$ aq. $+ H_2$, $\Delta H = -36{,}600$.

70. What is the hydrion concentration in a $0\cdot1N$ solution of CH_3COOH ($K = 1\cdot85 \times 10^{-5}$)? What vol. of $0\cdot1N$ Na acetate must be added to 1 l. of $0\cdot1N$ CH_3COOH in order to reduce the hydrion concentration to 10^{-5}? (Lond. Univ. Scholarships Exam., 1927.)

71. The osmotic pressure of a sucrose solution containing 680 g. per 1000 g. of H_2O is $57\cdot5$ atm. at 30°. Density measurements show that the solution contains $478\cdot3$ g. of sucrose per l. Calculate the O.P. of the solution according to the methods of van't Hoff and of Morse and Frazer.

72. If N_2O_4 is dissociated $80\cdot4$ per cent at $49\cdot7°$ and under a pressure of $93\cdot8$ mm., calculate the degree of dissociation at the same temperature and under a pressure of 200 mm.

73. The following table gives the dissociation pressures of CaH_2 at a series of temperatures:

T (°K.)	..	914	943	978	1001	1020
p (mm.)	..	0·5	1·2	3·0	5·1	8·0

Show that the heat of reaction is nearly constant, and calculate its value at 1000° K. (Manc. Hons. Chem., 1925.)

74. The percentage dissociation in the reaction $2H_2 + O_2 = 2H_2O$ is $0·0_4258$ at 1000° K. Calculate the standard affinity of the reaction per mol of water.

75. A solution containing 0·5042 g. of a non-volatile substance dissolved in 42·02 g. of C_6H_6 boils at 80·375° C. Find the mol. wt. of the solute, given that the b.p. of C_6H_6 is 80·200° C. and that its latent heat of evaporation is 94 cal./g. (Manc. Hons. Chem., 1920.)

76. If 2 l. of H_2O are shaken at 0° with 0·5 l. of O_2 in a closed vessel of 2·5 l. capacity, what is the partial pressure of the O_2 at equilibrium, the initial pressure being 750 mm.? Vapour pressure of $H_2O = 4·58$ mm. at 0°; solubility coefficient of O_2, 0·04924.

77. If an amount of base insufficient for complete saturation is added to an equimolecular mixture of acetic ($K = 1·8 \times 10^{-5}$) and glycollic ($K = 1·5 \times 10^{-4}$) acids, in what proportion will the salts be formed?

78. The E.M.F. of the cell $Ag/N AgNO_3//N ZnSO_4/Zn$ is 1·575 volt, the boundary potential between the solutions being eliminated. Calculate the resulting E.M.F. when the Ag solution is diluted to $0·001N$ and the Zn solution to $0·01N$, the following specific conductivities (ohm^{-1}) being given: N AgNO$_3$, 0·0675; $0·001N$ AgNO$_3$, 0·000113; N ZnSO$_4$, 0·0265; $0·01N$ ZnSO$_4$, 0·00073. (Manc. Hons. Chem., 1926.)

79. CH_3COOH is 1·34 per cent ionized in $N/10$ solution at 25°. What is the percentage ionization in a $N/100$ solution?

80. When 0·5 g. of a certain non-volatile solute was dissolved in 25 g. of C_6H_6, the b.p. of the latter was raised 0·40° C. When the atmospheric pressure is increased from 760 mm. to 770 mm. the b.p. of pure C_6H_6 is raised 0·45°. Find the approx. mol. wt. of the solute. (Manc. Hons. Chem., 1922.)

81. Calculate the maximum possible efficiency of a steam-engine receiving superheated steam at 180° C. and exhausting at 95° C.

82. Calculate the heat of solution of Zn in HCl, $100H_2O$ at 18° from the following: (i) $Zn + 3·112 (HCl, 20H_2O) = ZnCl_2, 4H_2O + 1·112 (HCl, 20H_2O) + H_2 + 0·0207 H_2O$ $(g.) + 32,795$ cal; (ii) $ZnCl_2$, $40H_2O + 1·112 (HCl, 20H_2O) + 560·16 H_2O = ZnCl_2$, $400H_2O + 1·112 (HCl, 200H_2O) + 5027$ cal.; (iii) $3·112 (HCl, 200H_2O) = 3·112 (HCl, 20H_2O) + 560·16 H_2O - 1719$ cal.; (iv) $3·112 (HCl, 20H_2O) + 0·0207 H_2O$ $(l.) = 3·112 (HCl, 20H_2O) + 0·06$ cal.; (v) $0·0207 H_2O$ $(g.) = 0·0207 H_2O$ $(l.) + 222$ cal.

83. A solution of H_2O_2 was treated with colloidal Pt and the vol.

of the O_2 evolved was noted at successive times with the following results:

Time from start (min.) ..	10	30	∞
Total volume (c.c.) ..	3·3	8·1	15·6

What is the order of the reaction? (Manc. Hons. Chem., 1922.)

84. The dissociation constant of H_2O, K_w, is $1·4 \times 10^{-14}$ at 25°. The heat of dissociation is given by $Q = 27,857·5 - 48·5\,T$ cal. per mol. Calculate K_w at 0°.

85. In 1 l. of a water solution saturated with CO_2 under 2·5 atm. pressure 0·444 mol of $MgCO_3$ dissolved. The Mg exists almost completely as $Mg(HCO_3)_2$, the degree of dissociation being 0·57. Using data in Exercise 33, p. 110, calculate the solubility product of $MgCO_3$.

86. A current of dry air was passed through a solution of 3·458 g. of a substance in 100 g. of EtOH, and then passed through EtOH alone. The loss in weight of the former liquid was 0·9675 g. and of the latter, 0·0255 g. Find the mol. wt. of the dissolved substance. (Manc. Hons. Chem., 1907.)

87. A saturated aqueous solution of $BaSO_4$ at 25° C. contains $2·3 \times 10^{-4}$ per cent of salt. Calculate the solubility product. What will be the solubility of $BaSO_4$ in $0·2N$ $(NH_4)_2SO_4$, assuming the latter to be completely dissociated?

88. The E.M.F. of the cell Ag/AgCl in $0·1N$ KCl/saturated $NH_4NO_3//0·1N$ $AgNO_3$/Ag is $-0·45$ volt at 25°; the degrees of dissociation are: KCl, 0·85; $AgNO_3$, 0·817. Calculate the solubility of AgCl in mol/l.

89. The transport number of Ag˙ in $AgNO_3$ is 0·476 and $\Lambda_\infty = 115·8$. What is the absolute velocity of Ag˙ in cm./sec. under unit potential gradient?

90. The reaction $H_2 + Cl_2 = 2HCl$ (g.) proceeds at room temperature with the evolution of 44,000 cal. Calculate the partial pressure of H_2 in the equilibrium mixture at 300° C. and 1 atm. Chemical constants on p. 130.

91. A solution containing 0·56292 per cent of $AgNO_3$ was electrolysed between Ag electrodes in a transport apparatus. After electrolysis the anode solution, which weighed 323·014 g., contained 0·67319 per cent of $AgNO_3$. 0·43380 g. of Ag was deposited in the coulometer. What is the transport number of Ag?

92. Equivalent quantities of I_2 and potassium phenyl propiolate were allowed to react, 25 c.c. of solution being withdrawn after t hr. and titrated with $0·1N$ $Na_2S_2O_3$ (x c.c.):

t ..	0	20	24	28	42
x ..	24·96	10·39	9·25	8·45	6·36

What is the order of the reaction?

93. A current of 0·85 amp. passing through a Pt resistance of 4·25 ohms embedded in benzophenone at the m.p. (48°) caused 35·66 g. of the latter to fuse in 17 min. 30 sec. Calculate Lf at the m.p.

94. Calculate the degree of dissociation of NH_4OH in $0.1N$ solution from the following data: Λ at $25° = 4$; Λ_∞ for $NH_4Cl = 155$; the transport number of $NH_4^{\cdot}$ is 0.50 in case of NH_4Cl and 0.27 in case of NH_4OH.

95. The specific conductivity of saturated Ag oxalate solution is 25.5×10^{-6} ohm^{-1}. Given the following mobilities: $Ag^{\cdot}$, 54.3; $\frac{1}{2}C_2O_4''$, 63, calculate the solubility of AgC_2O_4 in g./l. at $18°$.

96. At $25°$ $0.02N$ cumic acid is 4.88 per cent dissociated and $0.02N$ glycollic acid 8.3 per cent. What is the H-ion concentration in a mixture of 1 l. of the former solution with 1 l. of the latter?

How much potassium glycollate (completely dissociated) should be added to 1 l. of $0.02N$ glycollic acid in order to give it the H-ion concentration of a $0.02N$ cumic acid solution?

97. The E.M.F. of the cell Au (s), $Au_2O_3(s)/H_2SO_4$ solution/ Pt (H_2; 1 atm.) is 1.363 volts at $25°$. If the free energy of formation of liquid water at $25°$ is $-56,560$ cal./mol, calculate the free energy of formation of Au_2O_3 from Au and O_2 (g) at $25°$. Find also the dissociation pressure of Au_2O_3 at this temperature and, if the heat of formation of Au_2O_3 is $13,200$ cal./mol, calculate the entropy of formation of the oxide at $25°$. What conclusions can be drawn as to the stability of Au_2O_3?

98. The vapour pressures of Sr are as follow:

p (mm.)	..	9	84	201	535
t (°C.)	..	944	1057	1088	1138

Show that λ_e is approximately 79,200 cal. and the b.p. 1150° C.

99. If the maximum work of the reaction $\frac{1}{2}Br_2 + \frac{1}{2}H_2 = HBr$ is given by $A = 12,200 - RT \ln(p_{HBr}/\sqrt{p_{Br_2}p_{H_2}}) + 2T$, show that the degree of dissociation of HBr at 1000° K. is about 0.15 per cent.

100. Calculate the E.M.F. of the cell $Pt(H_2)/0.01N$ HCOOH// $0.005N$ MeCOOH/$Pt(H_2)$, if the dissociation constants of the acids are 1.3×10^{-3} and 1.8×10^{-5} respectively.

TABLES

(i) CONVERSION TABLE

(From Partington, *Chemical Thermodynamics*, p. 22)

—	Ergs.	Joules.	15° Cal.	l. atm.	g. cm.
1 erg =	1	10^{-7}	0.23901×10^{-7}	9.8692×10^{-10}	1.01977×10^{-3}
1 Joule =	10^7	1	0.23901	9.8692×10^{-3}	1.01977×10^4
1 15° Cal. =	4.184×10^7	4.184	1	4.129×10^{-2}	4.2667×10^4
1 l. atm. =	1.01325×10^9	101.325	24.22	1	1.0333×10^6
1 g. cm. =	9.80616×10^2	9.80616×10^{-5}	2.3437×10^{-5}	9.6777×10^{-7}	1

(ii) Atomic Weights (1927)

El.	Exact At. Wt.	Approx. At. Wt.	El.	Exact At. Wt.	Approx. At. Wt.	El.	Exact At. Wt.	Approx. At. Wt.
Ag	107·880	108	Cu	63·57	63·6	N	14·008	14
Al	26·97	27	F	19·00	19	Na	22·997	23
As	74·96	75	Fe	55·84	56	Ni	58·69	59
Au	197·2	197	Ga	69·72	70	O	16·000	16
B	10·82	11	Ge	72·60	72·6	P	31·027	31
Ba	137·37	137·4	H	1·008	1	Pb	207·22	207
Bi	209·00	209	He	4·000	4	Pt	195·23	195
Br	79·916	80	Hg	200·61	200	S	32·064	32
C	12·000	12	I	126·932	127	Sb	121·77	122
Ca	40·07	40	K	39·096	39	Se	79·2	79
Cd	112·41	112·4	Li	6·940	7	Si	28·06	28
Cl	35·457	35·5	Mg ·	24·32	24	Sn	118·70	119
Co	58·94	59	Mn	54·93	55	Sr	87·63	87·6
Cr	52·01	52	Mo	96·0	96	Zn	65·38	65·4

(iii) Mol Fractions, Mol Ratios, and Molalities
(From Lewis and Randall, *Thermodynamics*, p. 609)

N_2	N_2/N_1	M (of N_2)	N_2	N_2/N_1	M (of N_2)	N_2	N_2/N_1	M (of N_2)
0·005	0·005025	0·2789	0·040	0·04167	2·313	0·20	0·2500	13·88
·010	·01010	·5607	·045	·04712	2·616	·25	·3333	18·50
·015	·01523	·8453	·050	·05263	2·922	·30	·4286	23·79
·020	·02041	1·133	·075	·08108	4·501	·35	·5385	29·80
·025	·02564	1·423	·085	·09290	5·157	·40	·6667	37·01
·030	·03093	1·717	·100	·1111	6·168	·45	·8182	45·42
·035	·03627	2·013	·150	·1765	9·796	·50	1·0000	55·51

(iv) Vapour Pressure of Water
(From Partington, *Inorganic Chemistry*, p. 77)

° C.	p (mm.).	° C.	p (mm.).	° C.	p (mm.).	° C.	p (mm.).
0	4·579	17	14·530	30	31·824	93	588·60
5	6·543	18	15·477	40	55·324	94	610·90
10	9·209	19	16·477	50	92·51	95	633·90
11	9·844	20	17·535	60	149·38	96	657·62
12	10·518	21	18·650	70	233·7	97	682·07
13	11·231	22	19·827	80	355·1	98	707·27
14	11·987	23	21·068	90	525·76	99	733·24
15	12·788	24	22·377	91	546·05	100	760·00
16	13·634	25	23·756	92	566·99	110	1074·6

(v) Standard Electrode Potentials (25°)
(From Taylor, *Physical Chemistry*, Vol. II, p. 798)

Li·	.. −2·958	Fe··	.. −0·441	H·	.. ±0·0	Ag·	.. +0·800
Rb·	.. −2·924	Cd··	.. −0·398	Cu··	.. +0·345	H₂(OH′)	−0·828
K·	.. −2·922	Sn··	.. −0·136	O₂(OH′)	+0·398·	Br′	.. +1·066
Na·	.. −2·713	Pb··	.. −0·122	I′	+0·588	Cl′	.. +1·359
Zn··	.. −0·758	Fe···	.. −0·045	Hg₂··	.. +0·799	F′	.. +1·9

The values, in volts, refer to *unit activities* of the ions, with the sign convention of p. 113.

LOGARITHM TABLES

LOGARITHMS

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	9	13	17	21	26	30	34	38
											4	8	12	16	20	24	28	32	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	12	15	19	23	27	31	35
											4	7	11	15	19	22	26	30	33
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	11	14	18	21	25	28	32
											3	7	10	14	17	20	24	27	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	7	10	13	16	20	23	26	30
											3	7	10	12	16	19	22	25	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	28
											3	6	9	12	15	17	20	23	26
15	1761	1790	1818	1847	1875	1903	1 31	1959	1987	2014	3	6	9	11	14	17	20	23	26
											3	5	8	11	14	16	19	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	14	16	19	22	24
											3	5	8	10	13	15	18	21	23
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	3	5	8	10	13	15	18	20	23
											2	5	7	10	12	15	17	19	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
											2	5	7	9	11	14	16	18	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
											2	4	6	8	11	13	15	17	19
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8

LOGARITHMS

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

ANTILOGARITHMS

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
·00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0	0	1	1	1	1	2	2	2
·01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0	0	1	1	1	1	2	2	2
·02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0	0	1	1	1	1	2	2	2
·03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0	0	1	1	1	1	2	2	2
·04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0	1	1	1	1	2	2	2	2
·05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0	1	1	1	1	2	2	2	2
·06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0	1	1	1	1	2	2	2	2
·07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0	1	1	1	1	2	2	2	2
·08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0	1	1	1	1	2	2	2	3
·09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0	1	1	1	1	2	2	2	3
·10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0	1	1	1	1	2	2	2	3
·11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0	1	1	1	2	2	2	2	3
·12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0	1	1	1	2	2	2	3	3
·13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0	1	1	1	2	2	2	3	3
·14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0	1	1	1	2	2	2	3	3
·15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0	1	1	1	2	2	2	3	3
·16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0	1	1	1	2	2	2	3	3
·17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0	1	1	1	2	2	2	3	3
·18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0	1	1	1	2	2	2	3	3
·19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0	1	1	1	2	2	3	3	3
·20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0	1	1	1	2	2	3	3	3
·21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0	1	1	2	2	2	3	3	3
·22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0	1	1	2	2	2	3	3	3
·23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0	1	1	2	2	2	3	3	4
·24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0	1	1	2	2	2	3	3	4
·25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0	1	1	2	2	2	3	3	4
·26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0	1	1	2	2	3	3	3	4
·27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0	1	1	2	2	3	3	3	4
·28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0	1	1	2	2	3	3	4	4
·29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0	1	1	2	2	3	3	4	4
·30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0	1	1	2	2	3	3	4	4
·31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0	1	1	2	2	3	3	4	4
·32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0	1	1	2	2	3	3	4	4
·33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0	1	1	2	2	3	3	4	4
·34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1	1	2	2	3	3	4	4	5
·35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1	1	2	2	3	3	4	4	5
·36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1	1	2	2	3	3	4	4	5
·37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	1	1	2	2	3	3	4	4	5
·38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1	1	2	2	3	3	4	4	5
·39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1	1	2	2	3	3	4	5	5
·40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1	1	2	2	3	4	4	5	5
·41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1	1	2	2	3	4	4	5	5
·42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	1	1	2	2	3	4	4	5	6
·43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	1	1	2	3	3	4	4	5	6
·44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	1	1	2	3	3	4	4	5	6
·45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1	1	2	3	3	4	5	5	6
·46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1	1	2	3	3	4	5	5	6
·47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1	1	2	3	3	4	5	5	6
·48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1	1	2	3	4	4	5	6	6
·49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1	1	2	3	4	4	5	6	6

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	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
·50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	1	1	2	3	4	4	5	6	7
·51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	1	2	2	3	4	5	5	6	7
·52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	1	2	2	3	4	5	5	6	7
·53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	1	2	2	3	4	5	6	6	7
·54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	1	2	2	3	4	5	6	6	7
·55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	1	2	2	3	4	5	6	7	7
·56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	1	2	3	3	4	5	6	7	8
·57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	1	2	3	3	4	5	6	7	8
·58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	1	2	3	4	4	5	6	7	8
·59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	1	2	3	4	5	5	6	7	8
·60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	1	2	3	4	5	6	6	7	8
·61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	1	2	3	4	5	6	7	8	9
·62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	1	2	3	4	5	6	7	8	9
·63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1	2	3	4	5	6	7	8	9
·64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1	2	3	4	5	6	7	8	9
·65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	1	2	3	4	5	6	7	8	9
·66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	1	2	3	4	5	6	7	9	10
·67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	1	2	3	4	5	7	8	9	10
·68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	1	2	3	4	6	7	8	9	10
·69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	1	2	3	5	6	7	8	9	10
·70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	1	2	4	5	6	7	8	9	11
·71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	1	2	4	5	6	7	8	10	11
·72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	1	2	4	5	6	7	9	10	11
·73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	1	3	4	5	6	8	9	10	11
·74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	1	3	4	5	6	8	9	10	12
·75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1	3	4	5	7	8	9	10	12
·76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	1	3	4	5	7	8	9	11	12
·77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1	3	4	5	7	8	10	11	12
·78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	1	3	4	6	7	8	10	11	13
·79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	1	3	4	6	7	9	10	11	13
·80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	1	3	4	6	7	9	10	12	13
·81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	2	3	5	6	8	9	11	12	14
·82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	2	3	5	6	8	9	11	12	14
·83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2	3	5	6	8	9	11	13	14
·84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	10	11	13	15
·85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2	3	5	7	8	10	12	13	15
·86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2	3	5	7	8	10	12	13	15
·87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	3	5	7	9	10	12	14	16
·88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	11	12	14	16
·89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	5	7	9	11	13	14	16
·90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	6	7	9	11	13	15	17
·91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	9	11	13	15	17
·92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	10	12	14	15	17
·93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	2	4	6	8	10	12	14	16	18
·94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	10	12	14	16	18
·95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	2	4	6	8	10	12	15	17	19
·96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2	4	6	8	11	13	15	17	19
·97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2	4	7	9	11	13	15	17	20
·98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2	4	7	9	11	13	16	18	20
·99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	2	5	7	9	11	14	16	18	20

ANSWERS TO EXERCISES

Ex. I (p. 8).—**1.** $-131.7°$ C.; 1168 cal.   **2.** 59.28 l. atm.
3. 530° C.; 34.2 atm.   **4.** $\Delta v = 32.04$ l.; A $= 350.5$ cal.; 49.4° C.
5. -89.85 c.c.   **6.** 5/3.   **7.** -980 cal.   **8.** $C_p = 7.194$; $C_v = 5.207$.

Ex. II (p. 9).—**1.** 0.323.   **2.** 0.11.   **3.** 16,610 cal.; 8610 cal.

Ex. III (p. 12).—**1.** 0.1436.   **2.** $c = 0.1054 + 0.00007t$.   **3.** Put
$t_2 = t$ and $t_1 = 0$; $c = 0.232$.   **5.** $c = 0.067047 + 0.0_31569t -$
0.0_64176t^2; $c = 0.0802$ at 250°.   **6.** 0.033458.   **7.** 0.2839 cal.
8. 0.0043 cal./g.   **9.** 0.0156 cal./g.   **10.** 1.595×10^{-6}.   **11.** 1.037
$\times 10^{-2}$.   **12.** $c_p = 0.771$; $c_v = 0.651$.   **13.** 0.042.   **14.** 32.5 cal./g.
15. (i) 0.2086; (ii) 0.1043; (iii) 0.0905; (iv) 0.0532; (v) 0.0300.
16. 8.803; 6.761.

Ex. IV (p. 16).—**1.** (i) 5.72; (ii) 4.05; (iii) 5.66; (iv) 5.90; (v) 1.10.
2. 6.26.   **3.** 0.0725.   **4.** 11.74.   **5.** 9.82.   **6.** 6.46; 6.45.
7. 4.35×10^{12}.

Ex. V (p. 18).—**1.** 50.7 atm.   **2.** 33.5 cal.   **3.** 6.984 g./c.c.
4. $-0.03°$.   **5.** 13,300 cal./mol of O_2.

Ex. VI (p. 23).—**1.** 5337 cal.   **2.** 296.8 c.c.   **3.** 52.6 cal./g.
4. 2950 cal./mol; 160° K.   **5.** 217° C.   **6.** 1670 cal./mol; mean
$a = 2.737$.   **7.** (i) 183.7° K.; (ii) 3647.4 cal.; (iii) 3325 cal./mol.
8. 86.77° K.   **9.** 1020 mm.; 54.3°.   **10.** Constant $= 4.4$.   **11.** 357°
C.   **12.** 86.92° C.   **13.** 89.8° C.; 10° C.   **15.** $\lambda_e = 14,995.2 -$
$1.29583T$.   **16.** 24.7 cal./mol.   **17.** 14,700 cal./mol.   **18.** (a) 7750
cal./mol;   (b) $\lambda_e = 8331 - 10.133T$;   (c) $\lambda_e = 5778$;   (d) 245.2°
K.; $p = 552.2$ mm.; (e) 1904 cal./mol.   **19.** 42,500 cal./mol graphi-
cally and 39,700 cal. by (41).   **20.** 3460 cal./mol H_2O, evolved.

Ex. VII (p. 27).—**1.** (a) 12,000 cal./mol; (b) 20,400 cal./mol.
2. 97,690 cal./mol.   **3.** 103,170 cal./mol.   **4.** 18,670 cal./mol.
5. 160,980 cal./mol; 269,040 cal./mol.   **6.** 51,620 cal./mol.
7. 40,800 cal./mol.   **8.** 192,300 cal./mol.   **10.** 24,520 cal./mol.
11. 2570 cal. absorbed.   **12.** 4773 cal. evolved; 70 cal./mol ab-
sorbed.   **13.** 43,200 cal. absorbed per mol of S_8.

Ex. VIII (p. 30).—**1.** 7992 cal.   **2.** $Q_p = 21,931 + 0.202T +$
$0.0001T^2$; 22,350 cal. at 1273° K.   **3.** 46,256 cal. per 2NO.
4. 40,022 cal. absorbed.   **5.** 64,085 cal./mol of CO_2.   **6.** 67,570
cal./mol evolved.   **7.** $-10,200$ cal.; -6780 cal.

Ex. IX (p. 34).—**1**. 1·809 unit. **2**. 0·315 unit. **3**. 0·07 unit. **4**. 60·62 units. **5**. 0·4332 unit. **6**. 29·68 units. **7**. 0·974 unit per mol. **8**. 3·8 units.

Ex. X (p. 38).—**1**. 3510 cal. **2**. + 388 cal. **3**. 70,000 cal. **4**. 4630 cal.; 3926 cal. **6**. 53·17 l. atm. **7**. − 45,100 cal. **8**. 795 cal. **9**. $Q = 332 + 1·3675T − 0·004387T^2 + 0·0_5975T^3 − 8·1 \times 10^{-9}T^4$; $Q_{80} = 418$ cal.; $Q_{200} = 495$ cal.; $\Delta Z = 332 − 3·14T \log T + 4·4 \times 10^{-3}T^2 − 4·9 \times 10^{-6}T^3 + 2·7 \times 10^{-9}T^4 + 5·68T$. **11**. 94 cal. **12**. Less stable. **14**. − 53,664 cal.

Ex. XI (p. 43).—**1**. 768·4 mm. **2**. 781·7 mm. **3**. $CuSO_4$, $5H_2O$; $BaCl_2, 2H_2O$. **4**. 230°. **5**. 86·8 c.c. **6**. 70·33 mm. **7**. 0·04556 l. atm./1° F. **9**. 8·5 l. **10**. 0·0000115 cm. **11**. 0·0000222 cm. **12**. 0·00008 cm.

Ex. XII (p. 45).—**1**. 13·999. **2**. 79·919. **3**. 14·055. **4**. 32·092. **5**. 1·42761. **6**. 20·1565. **7**. 12·004. **8**. $p_0v_0/p_1v_1 = 1·00748$; 35·461. **9**. 0·02381. **10**. 50·55.

Ex. XIII (p. 48).—**1**. 1·749 atm. **2**. (i) 26·6; (ii) 37·09; (iii) 42·99; (iv) 134·6; (v) 56·29 c.c./mol. **3**. $a = 244,500$; $b = 26·6$ (c.c., atm., mol); 31·4° C. **4**. 73·15 atm.; 31·8° C. **5**. H_2, 27·6 × 10^{-9} cm.; Cl_2, 35·4 × 10^{-9} cm. **6**. 39·92 ($n = 0·04467$). **7**. 6·04. **8**. 24,236 c.c. **9**. 12·15. **10**. 4·7 × 10^{-8} cm. **11**. 44·13 ($n = 0·04482$).

Ex. XIV (p. 50).—**1**. 1·2°. **2**. 222·6° K. **3**. 320·4 atm. **4**. 1370° K.

Ex. XV (p. 53). — **1**. 21·31, 18·59, 15·73 dynes/cm.; not associated. **2**. 26·56, 23·63, 21·17, 17·16 dynes/cm.; 172·7. **3**. 3·48. **4**. 359·7° C. **5**. 16·03 ergs/cm.²; 232·6 ergs. **6**. 1·99. **7**. 4·63 × 10^{-10} mol/cm.². **9**. 5·5 × 10^{-8} g./cm.².

Ex. XVI (p. 55).—**1**. 19·83 atm.; 24 atm. **2**. 335·5 mm. **3**. 5·5 atm. **4**. 0·70. **5**. 29·53 atm.

Ex. XVII (p. 56).—**1**. 90·1. **2**. 41·09 atm. **3**. 14·92 mm. **4**. 238·2 **5**. 1·68. **6**. 42 atm.; 0·775. **7**. 132·4 atm. **8**. 4·28 mm.; 0·875.

Ex. XVIII (p. 58).—**1**. S_8. **2**. 123 cal./g. **3**. 0·554. **4**. 92·5 cal./g. **5**. 13 **6**. 0·68; 22·74 atm. **7**. 244. **8**. 216. **9**. 3·63 atm.

Ex. XIX (p. 60).—**1**. (i) 0·95; (ii) 0·913; (iii) 0·117; (iv) 0·8975; (v) 0·8798. **2**. $x = 2$. **3**. 3·085 per cent (P in 100 g. of solution) or 3·185 per cent (100 g. of solvent). **4**. (i) 0·479; (ii) 4·44 mm.; (iii) 55 atm.; (iv) 101·077°. **5**. 471. **6**. Mol. wt. = 233; completely associated to double mols. **7**. 4·216 mm. **8**. 0·096 atm. **10**. − 0·5018°; − 0·734°. **11**. 52·2 cal. **12**. 4·94° approx.; 48·6. **13**. 30 per cent naphthalene. **14**. 4·612 mm. **15**. 1·99 mm.

Ex. XX (p. 69). — **1**. $K_p = 2·85 \times 10^{-6}$; $K_c = 1·54 \times 10^{-8}$; p_{H_2O}, 0·9736 atm.; p_{O_2}, 0·0088. **2**. 0·212; 8·06 mm. 657·3 g. **3**. $K_p = 0·756[= 4x^2P/(1 − x^2)$ with p in atm.]; 431 mm.; 2·121 (air = 1). **4**. $K_p = 0·000567$; $K_c = 0·0465$. **5**. 97·8 per cent. **6**. 0·0_542 atm. **7**. 0·289 atm. **8**. 35 atm. **10**. $K_p = 1·6$; CO_2, 0·7; CO = H_2O, 9·4; H_2, 80·5. **11**. 98·6 per cent. **12**. 224·8 mm.; if P =

total pressure, $(P - p_{SO_2})^3 = p_{SO_2}{}^3 \times 42 \cdot 092 \, K_c T.$ **13.** $338 \cdot 9$ mm.
14. $0 \cdot 00015.$ **15.** $p = 1870(2 + 3\sqrt{K}) \, / \, 2(1 + \sqrt{K})^{1/2};$ 2120 mm.
16. $2 \times 10^{-0 \cdot 33}.$ **17.** $0 \cdot 594;$ $0 \cdot 00639.$

Ex. XXI (p. 73).—**1.** $43,470$ cal. (absorbed). **2.** $15,250$ cal.
(evolved). **3.** $20,100$ cal./mol $H_2S.$ **4.** $41,200$ cal. (absorbed) at
constant $p.$ **5.** $12,900$ cal. **6.** 4258 cal. / mol $NH_3;$ $0 \cdot 0169.$
7. $0 \cdot 00099.$ **8.** $0 \cdot 47.$ **9.** $0 \cdot 00031.$ **10.** 1×10^{-7} atm. **11.** $642 \cdot 9$
mm. **12.** $80,900$ cal./$2CO_2.$ **13.** $15,620$ cal./$H_2O.$ **14.** 5230 cal.
15. $- 2250$ cal. **16.** $10,470$ cal./$SnO;$ $20,265$ cal./$SnO_2.$ **17.** K_p
$= 1 \cdot 727.$ **18.** $\Delta Z = - 1270 + 0 \cdot 45 \, T \, \ln T - 0 \cdot 0_4 25 \, T^2 - 5 \, T.$
19. $\log p_{CO_2} \, / \, p_{CO}{}^2 = 8325 \, / \, T - 1 \cdot 78 \, \log T + 0 \cdot 0003387 \, T - 3 \cdot 589.$
20. $A = 16,300 - 6 \cdot 6 \, T \, \ln T - 0 \cdot 0008 \, T^2 + 0 \cdot 0_6 2 \, T^3 + 26 \cdot 0 \, T;$ A_{298}
$= 12,800$ cal.

Ex. XXII (p. 82).—**1.** Mean constant (in terms of c.c. of $Na_2S_2O_3$)
$0 \cdot 139.$ **3.** $\alpha = - 8 \cdot 38 + 33 \cdot 54(0 \cdot 4128)^{(t/176)};$ $+ 1 \cdot 86°.$ **4.** $k =$
$[\ln b(a + x) \, / \, a(b - x)] \, / \, t(a + b).$ **5.** Second. **7.** $k_1' + k_1'' =$
$[\log(r_0 - r_\infty) / (r - r_\infty)] \, / \, t = 0 \cdot 00187$ approx. **8.** $k_1'' = [\log(r_0 -$
$r_\infty) / (r - r_\infty)] / t = 0 \cdot 0007$ approx.; $\therefore$ $k_1' / k_1'' = 11 \cdot 7 / 7 = (82 \cdot 5 -$
$52 \cdot 5) / (52 \cdot 5 -$ specific rotation of lactone); $34.$ **9.** $dx / dt = k_1'(a -$
$x) - k_1''x.$ Let $\xi =$ value of x at equilibrium; then $k_1'' = k_1'$
$(a - \xi) / \xi,$ whence $1/t \cdot \log \xi / (\xi - x) = k_1' + k_1''.$ In terms of $y,$
$k_1' + k_1'' = 0 \cdot 00155.$ **10.** If $x = MeCOOH$ liberated in time t
then $\log b(a + x) / a(b - x) = k_1 t(a + b).$ The constant diminishes
owing to slow loss of Me acetate. **11.** First.

Ex. XXIII (p. 86).—**1.** $Cl_2.$ **2.** The last two; both require
$\sqrt{p/v} = k;$ $k = 1 \cdot 3.$ **3.** $s = 0 \cdot 58 / 27 \cdot 22 = 0 \cdot 0213;$ $\beta = 0 \cdot 0213 /$
$(1 + 0 \cdot 00367 \times 18 \cdot 5) = 0 \cdot 0199.$ **4.** $A,$ $177 \cdot 3$ mm.; $B,$ 538 mm.
5. $O_2,$ 234 mm.; $H_2,$ $238 \cdot 2$ mm.; $CO_2,$ $112 \cdot 2$ mm. **6.** $34 \cdot 7$ per
cent $O_2;$ $65 \cdot 3$ per cent $N_2.$ **7.** $1 \cdot 02 \times 10^{-6}.$

Ex. XXIV (p. 89).—**1.** $0 \cdot 00461$ g. **2.** $0 \cdot 0188.$ **3.** $35 \cdot 59.$
4. $1 \cdot 97.$ **5.** $2 \cdot 22$ per cent; $K_b = 1 \cdot 13 \times 10^{-9}.$ **6.** $5 \times 10^{-9}.$
8. If $\alpha =$ concentration of ester in dilute acid at any moment $t,$ then
$dx / dt = k\alpha$ and $\alpha v_2 / [(a - \alpha - x)v_1] = C.$

Ex. XXV (p. 93).—**1.** $0 \cdot 371$ g. ion/l. **2.** $4 \cdot 295$ ohm$^{-1}.$ **3.** $\Lambda =$
$90 \cdot 21$ ohm$^{-1};$ $\varkappa = 0 \cdot 00451$ ohm$^{-1}.$ **4.** $91 \cdot 46$ ohm$^{-1}.$ **5.** $94 \cdot 55$ cal.
6. $10 \cdot 36$ cal./g. **7.** 116 ohm$^{-1}.$ **8.** $115 \cdot 9$ ohm$^{-1}.$ **9.** $\Lambda_\infty =$
$130 \cdot 1$ ohm$^{-1}.$ **10.** $\Lambda_\infty = 108 \cdot 9$ ohm$^{-1}.$ **11.** $n = 1 \cdot 5;$ $\Lambda_\infty =$
$127 \cdot 5$ ohm$^{-1}.$

Ex. XXVI (p. 99).—**1.** $51 \cdot 4$ cal./g. **2.** $67 \cdot 17$ ohm$^{-1}.$ **4.** $8 \cdot 18 \times$
10^{-8} g. ion/l. **5.** $173 \cdot 6.$ **6.** 1 pt. in $425 \times 10^3.$ **7.** $1 \cdot 214 \times$
10^{-4} g./l. **8.** $5 \cdot 30 \times 10^{-4}$ cm./sec. **9.** $97 \cdot 2$ per cent. **10.** $0 \cdot 321.$
11. $0 \cdot 282.$ **12.** $0 \cdot 331.$ **13.** $0 \cdot 1567.$ **14.** $K_2CdI_4;$ transport
number of anion $= 0 \cdot 31.$ **15.** $0 \cdot 383.$ **16.** $0 \cdot 301.$

Ex. XXVII (p. 107).—**1.** 344 ohm$^{-1}.$ **2.** $1 \cdot 2 \times 10^{-4}.$ **3.** $0 \cdot 0123;$
$0 \cdot 268N.$ **4.** $[H^\cdot] = 0 \cdot 00167$ g. equiv./l.; $K = 1 \cdot 687 \times 10^{-5};$
$0 \cdot 00641$ g. equiv./l. **5.** $0 \cdot 003;$ $5 \cdot 32 \times 10^{-5}$ ohm$^{-1}.$ **6.** $0 \cdot 0541$
g. equiv./l. **7.** $0 \cdot 1257N.$ **8.** $0 \cdot 006252$ mol/l. **9.** Concentration
of $MeCOOH = 0 \cdot 868$ mol/l.; $v = 576$ c.c. Concentration of pro-
pionic acid $= 1 \cdot 176$ mol/l.; $v = 424$ c.c. **10.** $2 \cdot 275$ g. **11.** $1 \cdot 85$
$10 \times {}^{-4}$ mol/l. **12.** $0 \cdot 594$ mol/l. **13.** $MeCOOH,$ $7 \cdot 76;$ glycollic

acid, $1 \cdot 008$. **14.** Chloracetic acid, $1 \cdot 18$; acetic acid, $1 \cdot 89$. **15.** $688 \cdot 5$ c.c. of propionic acid ($c = 0 \cdot 7264$ mol/l.) and $311 \cdot 5$ c.c. of acetic acid ($c = 0 \cdot 6885$ mol/l.). **16.** $1 \cdot 23$. **17.** $x = 36 \times 10^{-6}$; ($[HCO_3'] = 9 \times 10^{-7}$ mol/l.). **18.** $0 \cdot 6 \times 10^{-6}$ ohm^{-1}. **19.** $1 \cdot 0165 \times 10^{-3}$ ohm^{-1} ($c' = 0 \cdot 00571$). **20.** $5 \cdot 679 \times 10^{-3}$ ohm^{-1} ($c' = 0 \cdot 0166$). **21.** $0 \cdot 01545$ ohm^{-1}. **23.** $0 \cdot 1765$ mol. **24.** $0 \cdot 004$. **25.** $- 1150$ cal./mol. **26.** $0 \cdot 0121$; $0 \cdot 00042$; $0 \cdot 177$; $0 \cdot 0078$. **27.** $21 \cdot 5 \times 10^{-10}$. **28.** 1×10^{-2}. **29.** $0 \cdot 0018$ mol/l. **30.** $0 \cdot 9$; $1 \cdot 5 \times 10^{-4}$. **31.** $61 \cdot 5$ per cent. Let K = ratio of solubility products = $0 \cdot 387$. If $x = [OH']$ and $y = [SO_4'']$ in mol/l., then $x^2 = Ky$ and $x + 2y = 0 \cdot 2$, whence $x = 0 \cdot 1231$ mol of OH' or $2 \cdot 831$ g. of Na and percentage yield = $2 \cdot 831 \times 100/23 \div 0 \cdot 2 = 61 \cdot 5$. **33.** $27 \cdot 45 \times 10^{-10}$. **34.** $0 \cdot 0055$. **35.** $1 \cdot 3 \times 10^{-11}$. **36.** $0 \cdot 066$. **37.** $0 \cdot 014$. **38.** 92 per cent. **39.** $6 \cdot 9$ g. **40.** $- 193$ cal. **42.** $0 \cdot 004$ mol. **43.** $0 \cdot 012$ mol/l. **44.** 1045×10^{-6} ohm^{-1}. **45.** 21,030 cal.

Ex. XXVIII (p. 123).—**1.** $Zn + 2AgCl = ZnCl_2 + 2Ag$; 49,520 cal. **2.** 82,300 cal. **3.** $- 2193$ cal.; $y = 1$. **4.** $2 \times 198,600$ joules. **5.** 495 cal. evolved. **6.** 39,200 cal./mol. **7.** $0 \cdot 032 \, v$. **8.** $0 \cdot 501$. **9.** $0 \cdot 09232 \, v$. **10.** $0 \cdot 034 \, v$. **11.** $+ 0 \cdot 1689 \, v$. **12.** 46,750 cal.; $Hg'' \rightleftharpoons Hg + 2\oplus$, $\therefore y = 2$. **13.** $1 \cdot 8$ per cent. **14.** $0 \cdot 000193$. **15.** $0 \cdot 3989 \, v$. **16.** $0 \cdot 7 \times 10^{-14}$. **17.** 3×10^{-53} atm. **18.** $0 \cdot 048 \, v$. ($y = 4$). **19.** 3×10^{-25}; 6×10^{-22} atm.; 14,250 cal./mol HgO. **20.** $4 \cdot 2 \times 10^{-67}$ atm.; $2730°$ K. (Use equation 135.) **21.** $(+) \, Ag/$ $Ag' / NO_2', NO_3'/NO(-)$; $E_{298}(NO_2' \rightarrow NO_3' + NO) = + 0 \cdot 800 - 0 \cdot 306 = 0 \cdot 494 \, v$. **22.** Acid solution: $E_1 = 1 \cdot 646 - RT/4F \cdot \ln p_{N_2}/$ $p_{NO}{}^2[H']^4$; alkaline solution: $E_1 = 0 \cdot 82 + RT/4F \cdot \ln p_{NO}{}^2/p_{N_2}{}^2[OH']^4$. **23.** $- 0 \cdot 3990 \, v$. **24.** $- 0 \cdot 758 \, v$. **25.** $1 \cdot 26 \, v$. **26.** $1 \cdot 5 \times 10^{-5}$. **27.** $1 \cdot 682 \, v$. The electrode reactions are: $2CO + 8OH' + 4\oplus$ $= 2CO_3'' + 4H_2O$; $O_2 + 2H_2O = 4OH' + 4\oplus$. Hence $y = 4$. If $p_{CO_2} = k_0[H_2CO_3]$ then $E = RT/4F \cdot \ln(K p_{CO}{}^2 p_{O_2}/p_{CO_2}{}^2) = RT/4F$ $(\ln K - 2 \ln k_0 K_w{}^2[CO_3'']/K_1 K_2[OH']^2 + 2 \ln p_{CO} + \ln p_{O_2}] = 1 \cdot 624 - 0 \cdot 029 \log[CO_3''] + 0 \cdot 058 \log[OH']$. **28.** $2590°$ K. **29.** Conversion does not occur (A = 0) when $p_{NO_2} = 10^{-15}([NO_3'] [NO_2'])^{1/2}/[OH']$ holds (at $25°$). Under ordinary conditions conversion is almost complete. **30.** Reaction ceases when $p_{N_2O_4} = 10^{13}$ atm. **31.** $n = 6$. **33.** $0 \cdot 2494 \, v$. **34.** $- 0 \cdot 045 \, v$. **35.** $0 \cdot 0477 v$; 1934 cal. (absorbed); $7 \cdot 37$ cal./$1°$; $- 262 \cdot 9$ cal.

Ex. XXIX (p. 128).—**1.** 243 cal. **2.** 2466 cal. **3.** 12,420 cal. **5.** $0 \cdot 478 \, v$. **6.** $1 \cdot 459 \, v$. **7.** $366°$ K.

Ex. XXX (p. 131).—**1.** $236°$ C. **2.** $0 \cdot 1$ per cent of N_2 converted to NO. **3.** $2 \cdot 4 \times 10^{-67}$ atm.; $2345°$ K. **4.** $\log K = 5 \cdot 33$. **8.** $526°$ K. **9.** $0 \cdot 23$ atm. **10.** $0 \cdot 004$ per cent. **11.** $0 \cdot 2$ atm. **12.** 7×10^{-6} atm.